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The Reactions of Deuterium Atoms with Methane and Ethane

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The reactions of deuterium atoms with methane and ethane have been investigated, the atoms being produced by the discharge tube method and by photosensitization with mercury. The activation energies found were 11.7 Kcal. for methane, and 6.3 Kcal. for ethane.

The mechanism of the latter reaction is discussed, and it is concluded that the measured activation energy is that of the reaction

$$D+C_2H_6=C_2H_5+HD.$$

Hence the reaction

$$H+C_2H_6=C_2H_5+H_2$$

must have approximately the same energy of activation. On this assumption the free radical chain theory of first order reactions is discussed in the light of the recent work of Patat and Sachsse.

INTRODUCTION

SINCE the discovery of the heavy hydrogen isotope, the kinetics of a considerable number of exchange reactions have been investigated. Reactions involving atoms are among the most interesting of this type, and an investigation of the reactions of deuterium atoms with water, ammonia, acetylene, and methane has already been described.[1] In this investigation high concentrations of deuterium atoms, produced by the Wood-Bonhoeffer method,[2] were used and the following activation energies were found:

$D+H_2O$	11 Kcal.
$D+NH_3$	11 Kcal.
$D+C_2H_2$	$<$ 5 Kcal.
$D+CH_4$	$>$11 Kcal.

Prior to the publication of the above results, a note appeared by Taylor, Morikawa, and Benedict[3] describing an investigation of the reaction between deuterium atoms and methane. In their experiments the atomic deuterium was produced by photosensitization with mercury. They state that the activation energy of the reaction is of the order of 5 Kcal., which is in sharp contrast to our value of $>$11 Kcal.

In view of the discrepancy it was considered desirable to reinvestigate the reactions of deuterium atoms with saturated hydrocarbons. We have therefore investigated the reaction with ethane by the Wood-Bonhoeffer method, and the reactions with methane and with ethane by photosensitization with mercury.

A. EXPERIMENTS WITH DEUTERIUM ATOMS PRODUCED BY A DISCHARGE

The apparatus employed was of the usual type, hydrogen being run at very high rates of flow through a discharge tube, the atomic hydrogen thus produced being mixed with the other reactant, and the products removed from the flowing stream and later analysed. The apparatus was, in the main, similar to that previously employed.[1]

[1] Geib and Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935); Trans. Roy. Soc. Can. **3**, 91 (1935).
[2] Bonhoeffer, Zeits. f. physik. Chemie **113**, 199 (1924); **116**, 391 (1925).
[3] Taylor, Morikawa and Benedict, J. Am. Chem. Soc. **57**, 383 (1935).

The discharge was operated on alternating current at about 3000 volts, the current through the tube being maintained constant at 325 milliamperes. Deuterium was stored in a gas-holder at atmospheric pressure, and entered the system through calibrated capillary flow-meters. It passed through the discharge at a streaming velocity of about 1 liter per second, and a pressure of about 0.3 mm, and entered a reaction vessel of about 1 liter capacity. In this vessel it was mixed with the other reactant, and after a contact time of about 1 second the mixture passed out of the reaction vessel and over some gold foil which destroyed the remaining deuterium atoms. The walls of the discharge tube and the reaction vessel were coated with phosphoric acid in the usual way to cut down the rate of recombination of the atoms. The pumping system consisted of a three stage diffusion pump backed by an oil pump. The speed at the entrance to the pump was about 20 liters per second.

Runs were comparatively short in order to conserve deuterium. For this reason the atom concentration in the reaction vessel was determined indirectly by calibrating the apparatus with ordinary hydrogen, and the atom concentration of the deuterium in an experiment was inferred from the current flowing through the discharge. The calibration was made with a Wrede diffusion gauge.[4] The average atom concentration in a number of calibration runs was 20 percent.

After the gases had passed through the reaction vessel it was necessary to separate the methane or ethane from the deuterium. The vapor pressures at liquid air temperature were too high to permit a simple freezing out. Also, it was impossible to introduce an adsorbent into the main vacuum line, since the resistance thus introduced would cut down the pumping speed enormously. The reactants were therefore separated by adsorption on silica or alumina gel at $-180°$ in a trap between the diffusion pump and the oil pump. Blank runs showed that methane and ethane could be very efficiently separated from hydrogen in this way. After separation the gas was desorbed by warming the gel to $-80°$, and was allowed to expand into a combustion vessel where it was burned in dry air on a platinum filament. Since the desorption was carried out at $-80°$, there was no danger of contamination from traces of residual water which might have been present in the gel. The deuterium content of the resulting water was then determined by measuring the heat conductivity of the saturated vapor as previously described.[1]

Deuterium was prepared by the electrolysis of alkaline heavy water. It was passed through a tube filled with platinized asbestos at 500° to remove oxygen, dried by passage through a liquid air trap, and stored in a gas-holder over mercury. Methane and ethane were procured in cylinders from the Ohio Chemical Co. Ethane was purified by repeated fractional distillation. Methane was passed through ammoniacal cuprous chloride, dilute and concentrated sulphuric acid, a 50 cm column of copper oxide at 300°, concentrated potassium hydroxide solution, and Fieser's solution. It was then dried by passage through a trap at $-80°$, and repeatedly distilled. Acetylene was prepared from calcium carbide and water, washed with sodium hydroxide, and fractionally distilled.

Results with ethane

The results for ethane are given in Table I. The calculations were made as described in the previous papers. In column 5 is given the average time during which a molecule of the reactant is in the reaction space. This is calculated from a knowledge of the amount of gas flowing, the pressure in the reaction vessel, and the volume (920 cc) and temperature (20°) of the reaction vessel. A correction is applied for the increase in volume due to the fact that some of the hydrogen is present as atoms. $Z_{C_2H_6, D}$ in column 7 represents the average number of collisions of 1 ethane molecule with deuterium atoms during the time it is in the reaction vessel. It is calculated assuming a molecular diameter of 3.75×10^{-8} cm for ethane, and of 2.14×10^{-8} cm for a deuterium atom (assumed equal to the collision diameter of a hydrogen atom as found by Harteck).[5] The values of the "percent

[4] Wrede, Zeits. f. Instrumentenk **48**, 201 (1928); Harteck, Zeits. f. physik. Chemie **A139**, 98 (1928).

[5] Harteck, Zeits. f. physik. Chemie **A139**, 98 (1928).

TABLE I. *The reaction of deuterium atoms with ethane.*

Run No.	Remarks	Pressure (mm)	C_2H_6, cc/sec. at N.T.P.	Reaction Time (sec.)	P_D (cm)	$Z_{C_2H_6, D}$ ($\times 10^{-6}$)	% D Content of ethane	% Exchange	Collision Yield ($\times 10^6$)	E (cal.)
	DEUTERIUM FLOW = 0.202 cc/sec. at N.T.P.		AVERAGE ATOM CONTENT = 20%							
1	Blank, no discharge	0.27	0.049	1.11	—	—	0.0	0.0	—	—
2	.....	0.28	0.049	1.15	0.0046	7.8	10.7	18.5	1.5	6400
3	Blank, ethane alone, D_2 through discharge later	—	0.047	—	—	—	0.0	0.0	—	—
4	.....	0.28	0.044	1.17	0.0047	8.3	14.4	23.7	1.7	6350
5	.....	0.28	0.044	1.17	0.0047	8.3	16.4	27.0	2.0	6250
6	.....	0.28	0.037	1.20	0.0048	8.5	19.8	30.6	2.2	6200
7	.....	0.28	0.034	1.22	0.0048	8.5	17.9	27.0	1.9	6300
8	Blank, D_2 through discharge alone, ethane later	—	0.033	—	—	—	1.0	1.5	—	
										mean = 6300

exchange" in column 9 are calculated on the assumption that at equilibrium the distribution coefficient

$$\frac{\text{D/H in ethane}}{\text{D/H in hydrogen}} = 1.$$

In calculating the collision yields in column 10 allowance has been made for the fact that 6 fruitful collisions are required to convert a molecule of C_2H_6 to C_2D_6. The activation energies in the last column are calculated assuming a steric factor of 0.1.

The results lead to an activation energy for the exchange reaction of about 6300 calories. This is much lower than the value for methane, >11 Kcal., previously obtained. This is not surprising in view of the fact that methane has been previously reported to be without appreciable effect on hydrogen atoms, while ethane "catalytically" destroys them to a considerable extent.[6]

Results with methane-acetylene mixtures

It was shown in the previous paper by Geib and one of us[1] that the reaction $D+C_2H_2$ had a very low activation energy, *viz.* $\lesssim$4500 calories. On the basis of the discussion in a later section, it seems almost certain that the main primary reaction is

$$D+C_2H_2=C_2H+HD.$$

The reaction between deuterium atoms and methane, however, has a high activation energy and consequently shows no exchange with deuterium atoms under our experimental conditions. It therefore appeared possible that some information might be obtained by bringing together deuterium atoms and a mixture of methane and acetylene, and determining whether the reaction

$$C_2H+CH_4=C_2H_2+CH_3$$

occurred. If it did we would then have

$$CH_3+D(+M)=CH_3D,$$

and the methane should be partially exchanged.

The experimental procedure was identical with that previously described, except that the gases leaving the reaction vessel were first passed through two liquid air traps to freeze out the acetylene. The methane was then frozen out with silica gel as before, burned, and the water analyzed. The acetylene was burned and analyzed in a few cases. It may, however, have been contaminated with some dissolved methane. Since the methane was taken out last, however, there was no danger of it being contaminated with acetylene.

The results are given in Table II. It is evident that a small apparent exchange takes place. This, however, is of the same order of magnitude as in the run with methane alone, and in the previous investigation. It is also independent of

[6] v. Wartenberg and Schultze, Zeits. f. physik. Chemie B2, 1 (1929).

TABLE II. *Methane-acetylene mixtures.*

Run No.	Remarks	Pressure (mm)	CH_4 cc/sec. at N.T.P.	C_2H_2 cc/sec. at N.T.P.	% D Content of Methane	% D Content of Acetylene
9	Methane only	0.31	0.053	0.0	1.9	—
10	Acetylene only	0.29	0.0	0.049	—	38.7
11		0.30	0.040	0.013	2.9	38.7
12		0.28	0.028	0.010	2.9	31.4
13		0.27	0.013	0.017	2.5	—
14		0.27	0.0062	0.018	2.2	—
15	Blank, no discharge	0.27	0.0052	0.015	0.5	—

the C_2H_2/CH_4 ratio, which was varied over fairly wide limits. It therefore seems certain that the effect is due merely to a small amount of impurity in the methane. Hence, within the experimental error, the reaction

$$C_2H+CH_4=C_2H_2+CH_3$$

does not occur. The reaction therefore has an activation energy greater than about 8000 cal., in agreement with previous assumptions about reactions of this type.

B. Deuterium Atoms Produced by Photosensitization

The apparatus employed was of the usual static type. The reaction vessel, a cylindrical fused quartz bulb of about 140 cc capacity, was arranged so that measured amounts of various gases could be introduced and the pressure could be continuously observed. It contained a small pool of mercury. The vessel was immersed in a thermostat filled with distilled water at 23°C.

The light source was a Hanovia Resonance Lamp, consuming 100 milliamperes at about 5000 volts. With this lamp almost all the emitted light is in the resonance line at 2537A. The light passed through a quartz tube, cemented into the side of the thermostat, filled with acetic acid solution. The tube thus acted as a window, a condensing lens, and a filter. This arrangement was not very efficient, and reflection losses from the cylindrical vessel were high. As a result the intensity was low considering the source used, and rather long exposures were necessary.

The intensity of the absorbed light was inferred from measurements of the rate of the mercury photosensitized combination of hydrogen and oxygen under identical conditions. It was assumed that 5 molecules of (hydrogen +oxygen) disappeared per quantum of light absorbed.[7] An average value of 8.77×10^{12} quanta per cc per sec. was found.

In general deuterium was in considerable excess, the experimental mixture being usually about $4D_2+1CH_4$. The total pressure was in the neighborhood of 60 cm. After illumination the reactant was separated from the hydrogen, burned, and the deuterium content of the water determined as before.

As mentioned in the previous section, efficient separations of methane or ethane from hydrogen could be made by adsorption on silica gel at −180°. These had been accomplished in a flow system at moderately low pressures. At first it was not realized how sensitive the method was to experimental conditions, and the products were separated as follows:

(A) The methane-hydrogen mixture was kept in contact with alumina gel at −180° for 10 minutes. The system was then evacuated with an oil pump for 10 minutes, and the gel was warmed to −80° to desorb the methane.

(B) As in (A) but using silica gel.

These procedures gave rather high blank values, i.e., accomplished only a partial separation, as is shown by Table III, so the technique was modified as follows:

(C) The gases were pumped through silica gel at −180°, and the pumping was continued for 10 minutes. The methane was desorbed at −80° as before.

(D) As in (C) but using higher pumping speeds.

The separations thus effected were quite satisfactory, the blanks being reduced to about 2 percent.

The results for methane are given in Table III.

In order to calculate the collision yield, and hence the activation energy, it is first necessary to evaluate the stationary concentration of deuterium atoms produced by the illumination. The initial reactions

$$Hg+h\nu=Hg^*$$
$$Hg^*+D_2=Hg+2D$$

have been directly evaluated, since we have used the hydrogen-oxygen reaction as an actinometer. We may assume that the quenching effect of methane is negligible.[8] The wall deactivation of excited mercury atoms is also

[7] See, for example, Jungers and Taylor, J. Chem. Phys. **3**, 338 (1935).

[8] Zemansky, Phys. Rev. **36**, 919 (1930).

negligible for the gas pressures employed. The initial process will be followed by

(1) $D+D+M=D_2+M$

(2) $D=\frac{1}{2}D_2$ (wall)

(3) $D+CH_4=CH_3D+H$ (or other products which use up D atoms).

We may neglect the reaction $H+D+M=HD+M$, since for small percentage conversions there will be an inappreciable quantity of atomic hydrogen present. Hence we may write

$$\frac{d}{dt}[D]=\frac{2I_{abs.}}{N}-K_1[D]^2[M]-K_2\frac{[D]}{[M]}-K_3[D][CH_4]=0,$$

where N is Avogadro's number, and M is a third body.

The rate of recombination of hydrogen atoms under directly comparable experimental conditions has been investigated by Farkas and Sachsse,[9] who found that at pressures higher than 20 cm the term $K_2[H]/[M]$ could be neglected, and estimated K_1 (for H atoms) to be 3.4×10^{16} cm^6 mole^{-2} sec.$^{-1}$. There is a marked discrepancy between this result and those obtained by discharge tube methods.[10] In Farkas and Sachsse's experiments the rate constant given is based on the assumption that "M" is H_2. Smallwood found 1.7×10^{16} for the case where M is a hydrogen atom, and stated that the constant for the reaction $H+H+H_2$ was at least 50 times smaller. The two values for the latter reaction differ, therefore, by a factor of 100. The conditions in the two investigations were, however, widely different, since Farkas and Sachsse worked at pressures of the order of atmospheric and used minute H atom concentrations, while the other investigations were made with high H atom concentrations and pressures of the order of a millimeter.

Since the conditions in our experiments were almost identical with those of Farkas and Sachsse, we will adopt their value for the rate constant of the reaction $H+H+H_2$. It should be noted that Farkas and Sachsse *measured* the stationary hydrogen atom concentration and calculated the rate constant from it. Since we are using their values of the rate constant to calculate the stationary hydrogen atom concentration under almost identical conditions, we are in effect merely using their measured values of the hydrogen atom concentration. The values calculated in this way should therefore be but slightly influenced by any errors in Farkas and Sachsse's mechanism and calculations, and dependent only on the accuracy of their measurements of the stationary hydrogen atom concentration.

The above discussion refers, of course, to hydrogen, not deuterium. It may be assumed that the only difference between the two will be in the frequency of triple collisions. Tolman[11]

[9] Farkas and Sachsse, Zeits. f. physik. Chemie **B27**, 111 (1935).

[10] Amdur and Robinson, J. Am. Chem. Soc. **55**, 1395 (1933); Smallwood, ibid., **56**, 1542 (1934).

[11] Tolman, *Statistical Mechanics* (Chemical Catalog Co., New York), p. 245.

TABLE III. *The photosensitized reaction between deuterium and methane.* Temperature 23°C.

Run No.	Time of Illumination (sec.)	P_{D_2} (cm)	P_{CH_4} (cm)	Method of Analysis	D Content of Methane (%)	D Atom Concentration (moles/cc)	Fraction of Methane Converted per sec.	E (Kcal.)
1	0.95×10^5	39.6	9.5	A	4.5	$\sim6\times10^{-12}$	$<10^{-6}$	>11
2	0	37.5	10.5	A	6	—	—	—
3	4.08×10^5	45.0	10.0	B	11.5	5.8×10^{-12}	4.5×10^{-7}	11.6
4	1.58×10^5	52.5	12.5	B	4.5	$\sim6\times10^{-12}$	$<10^{-6}$	>11
5	3.81×10^5	39.2	14.4	B	6	$\sim6\times10^{-12}$	$<10^{-6}$	>11
6	0	39.0	13.0	B	7	—	—	—
7	0	40.0	14.0	C	3	—	—	—
8	5.68×10^5	39.6	10.8	C	6	6.5×10^{-12}	2.5×10^{-7}	12.0
9	0	39.8	11.2	C	2	—	—	—
10	0	42.2	11.3	D	1	—	—	—
11	2.25×10^5	38.9	12.6	D	4.5	6.1×10^{-12}	6.0×10^{-7}	11.4

has calculated the number of effective triple collisions in a mixture of perfect gases for the case where molecules of kinds (1) and (3) will react if they come within a distance δ of a molecule of kind (2). The result is

$$Z=8\sqrt{2}\pi^{\frac{1}{2}}N_1N_2N_3\sigma_{12}^2\sigma_{23}^2\delta(kT)^{\frac{1}{2}}\left(\frac{1}{(\mu_{23})^{\frac{1}{2}}}+\frac{1}{(\mu_{12})^{\frac{1}{2}}}\right),$$

where the N's refer to the number of molecules per cc of each type, the σ's to the average molecular diameters, and the μ's to the reduced masses. It follows from this that the reaction H+H+M should be $\sqrt{2}$ times faster than D+D+M,[12] the result being the same for an atomic or a molecular third body. Hence for deuterium atoms we will assume

$$K_1=(3.4\times10^{16})/1.41=2.4\times10^{16}.$$

We thus have the necessary data to calculate the stationary D atom concentration and the collision efficiency of reaction (3). If α is the fraction of CH_4 reacting per second, then

$$[\mathrm{D}]=\left(\frac{(2I_{\mathrm{abs.}}/N)-\alpha[\mathrm{CH_4}]}{K_1[\mathrm{M}]}\right)^{\frac{1}{2}},$$

and the collision yield of reaction (3) is

$$\alpha/b[\mathrm{D}],$$

where b is a collision factor having the value 3.0×10^{14} sec.$^{-1}$ mole^{-1} cm^3. This is calculated assuming the diameter of the methane molecule to be 3.75×10^{-8} cm.

In calculating E from the collision yield a steric factor of 0.1 has been assumed in conformity with the usual practice. The back reaction has been neglected, since its effect is negligible at small percentage conversions.

On account of the analytical difficulties previously mentioned, the data for runs 1 to 6 are merely qualitative. Nevertheless they serve to set a lower limit for the activation energy. For, even if the blank correction were omitted entirely, values of approximately 11 Kcal. would be obtained. In the last runs, where the blank corrections are smaller, a measurable exchange is established, and we obtain more definite values for the activation energy.

Preliminary measurements have also been made with ethane and deuterium. These indicate, in agreement with the results of the first section, that the activation energy of the reaction is much lower than that of the reaction with methane.

Discussion

(a) The reaction between deuterium atoms and methane

Our results indicate a value of 11.7 Kcal. for the photosensitized reaction. This is in complete agreement with the value of >11 Kcal. previously found by Geib and one of us by the discharge tube method.

Recently Farkas[13] has investigated the thermal reaction between deuterium atoms and ammonia. He finds an activation energy of 11±1 Kcal. At 1000°K his rate for D atoms and methane in some preliminary experiments is 6 times that for ammonia. Hence the activation energy must be almost the same, since there is no reason to assume a very different steric factor. His results are therefore in agreement with our findings.

It must therefore be concluded that the value of about 5 Kcal. reported by Taylor, Morikawa, and Benedict[3] is much too low. In the absence of a detailed account of their work, we are unable to suggest any explanation of the discrepancy.

Farkas finds a different order of reactivity for the series D+NH_3, H_2O, CH_4 than was found previously by Geib and one of us. This, however, is obviously due to the fact that, as we pointed out, some wall effects were undoubtedly occurring in the reactions with ammonia and water. These thus appeared somewhat faster than the methane reaction, whereas Farkas finds them to be somewhat slower. Our values of the activation energies, however, are in excellent agreement.

There seems to be no doubt that all these reactions proceed by a direct atomic metathesis analogous to the ortho-para hydrogen conversion, *viz.*

$$\mathrm{D+CH_4=CH_3D+H}.$$

[12] This relation has been confirmed experimentally by Amdur (J. Am. Chem. Soc. **57**, 856 (1935)), using a discharge tube method. He concluded, however, that atoms, not molecules, were the effective third bodies.

[13] Farkas, J. Chem. Soc. 26 (1936).

(b) The reaction between deuterium atoms and ethane

As we have shown, this reaction has a much lower activation energy, in the neighborhood of 6.3 Kcal. There are three main possibilities for the mechanism of the reaction:

I. Hydrogenation

(a) $C_2H_6+D = C_2H_6D$
(b) $C_2H_6D+D = C_2H_6+D_2$
or $= C_2H_5D+HD$

II. Dehydrogenation

(a) $C_2H_6+D = C_2H_5+HD$
(b) $C_2H_5+D = C_2H_5D$

III. Exchange by Metathesis

$C_2H_6+D = C_2H_5D+H.$

Mechanism *III* is undoubtedly the correct one for the reactions of deuterium atoms with methane, ammonia, etc., as described above. However, in view of the fact that ethane and acetylene are known to have a strong "catalytic" effect in destroying hydrogen atoms,[6] some other mechanism must exist, since *III* regenerates one hydrogen atom for each one destroyed and hence cannot account for a catalytic recombination. Furthermore the activation energies of the reactions with ethane and acetylene are so much lower than those for methane, ammonia, and water that it is obvious that the mechanisms must be distinctly different.

Mechanism *I* is very unlikely, since *I* (a) would presumably have to occur at a triple collision. This would make the reaction far too slow to enable ethane to exert a strong catalytic effect on the recombination of hydrogen atoms. Furthermore, even if *I* (a) occurred sufficiently rapidly, the very unstable molecule C_2H_6D would have little chance of surviving long enough (10^{-6} sec.) to meet a D atom and give *I* (b). Hence in general we would expect *I* (a) to be followed by

$$C_2H_6D = C_2H_5+HD$$
$$\text{or} = C_2H_4D+H_2,$$

which would make the whole process indistinguishable from *II* (a), or else by

$$C_2H_6D = C_2H_5D+H,$$

which would give a result indistinguishable from *III*.

Hence we must conclude that *II* is the correct mechanism, and that the measured heat of activation (6.3 Kcal.) is that of the reaction

$$C_2H_6+D = C_2H_5+HD,$$

and hence the companion reaction

$$C_2H_6+H = C_2H_5+H_2$$

also has an activation energy of the same order of magnitude.

The activation energy of the latter reaction is of very considerable importance from the point of view of the mechanism of the decomposition of gaseous organic compounds. The Rice free radical theory[14] has given a very satisfactory explanation of the products of organic decompositions. The theory has been extended to first order reactions, and it has been suggested that the majority of these occur by chain mechanisms.[15] These mechanisms are very attractive in principle, and they have received support from the fact that the introduction of free radicals into a vessel containing an organic substance may cause chains to be set up.[16] This, however, merely shows that chains *can* be set up by free radicals, and does not prove that free radicals are present and actually do set up chains during the normal slow decomposition of the substances concerned.

Recently the work of Patat and Sachsse[17] has thrown considerable doubt on the idea that most organic decompositions proceed by a radical chain mechanism. They measured the rate of the ortho-para hydrogen conversion in the presence of decomposing organic compounds, and were thus able to detect hydrogen atoms produced by the decomposition, or by the reaction

$$CH_3+H_2 = CH_4+H. \qquad (A)$$

In general the hydrogen atoms produced in this way are being destroyed by the reaction

$$H+RH = H_2+R, \qquad (B)$$

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[14] Rice and Rice, *The Aliphatic Free Radicals* (Baltimore, 1935).
[15] Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[16] Frey, Ind. Eng. Chem. **26**, 200 (1934); Allen and Sickman, J. Am. Chem. Soc. **56**, 1251, 2031 (1934); Leermakers, ibid. **56**, 1899 (1934).
[17] Patat and Sachsse, Nach. Ges. Wiss. Göttingen, [III] **1**, 41 (1935); Naturwiss. **23**, 247 (1935); Zeits. f. physik. Chemie **B31**, 105 (1935); Sachsse, ibid. **B31** 79 (1935).

where RH is an organic molecule and R a free radical. Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get

$$\frac{[CH_3]}{[H]} \sim \frac{K_B[RH]}{K_A[H_2]}.$$

Having evaluated [H] by means of the ortho-para hydrogen conversion, we can thus calculate $[CH_3]$ and compare it with the value calculated from the Rice-Herzfeld mechanism. In general, using the activation energies assigned to the above reactions by Rice and Herzfeld, Patat and Sachsse find the hydrogen atom concentrations to be several powers of 10 lower than those calculated from the free radical chain theory. Thus for the decomposition of ethane the Rice-Herzfeld mechanism is

		E, Kcal.
(1)	$C_2H_6=2CH_3$	80
(2)	$CH_3+C_2H_6=CH_4+C_2H_5$	20
(3)	$C_2H_5=C_2H_4+H$	49
(4)	$H+C_2H_6=H_2+C_2H_5$	17
(5)	$H+H=H_2$	Triple collision
(6)	$H+C_2H_5=C_2H_4+H_2$ (or C_2H_6)	small
(7)	$H+CH_3=CH_4$	small
(8)	$CH_3+C_2H_5=C_3H_8$	8
(9)	$2C_2H_5=C_4H_{10}$	8

If reactions (5), (7), (8) and (9) are assumed to be negligible, this gives a first order rate and good agreement with the observed value of the activation energy. Furthermore we obtain approximately

$$\frac{[CH_3]}{[H]} = \frac{K_4[C_2H_6]}{K_A[H_2]}.$$

Patat and Sachsse found, using $K_4=17$ Kcal. as given by Rice and Herzfeld, that the observed hydrogen atom concentration is about 1000 times too small.

Now, as pointed out above, the present investigation indicates that the activation energy of reaction (4) is about 6 Kcal. instead of 17 Kcal. There are also theoretical grounds for believing that 17 Kcal. is much too high.[18] If we calculate [H] using 6 Kcal. for this reaction, then the value obtained agrees almost exactly with that found by Patat and Sachsse. It thus appears that if we accept the value of 6 Kcal. found by us as being the activation energy of the reaction

$$H+C_2H_6=C_2H_5+H_2,$$

then the objections to the free radical scheme from the point of view of the stationary hydrogen atom concentration no longer hold. The same is true for most of the other free radical chain mechanisms if we assume that all the Rice-Herzfeld activation energies are too high for reactions of the type

$$H+RH=H_2+R.$$

Such a change in the activation energy of reaction (4), however, seems to introduce insurmountable difficulties into the application of the scheme to first order reactions. Thus in the case of ethane the fundamental reactions are (1), (2), (3) and (4), and these cannot be altered without virtually abandoning the entire free radical theory. As we have seen the change in E_4 brings the results into line with the work of Patat and Sachsse as far as the stationary hydrogen atom concentration is concerned. The overall order of the reaction and the theoretical value of E, however, are largely dependent on the manner in which the chains are terminated. The change in E_4 by altering the relative concentrations of the reacting substances upsets the relationships between the rate constants and it is no longer permissible to neglect reactions (8) and (9). Under these circumstances the scheme no longer predicts a first order rate or the correct value of the overall activation energy.

[18] London, Zeits. f. Elektrochem. **35**, 552 (1929).

The Absorption Spectrum of Methyl Alcohol Vapor in the Photographic Infrared*

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(Received May 18, 1936)

The absorption of methyl alcohol vapor in the photographic infrared has been explored under low dispersion. Absorption regions were found at λ9500 and λ7300, which correspond to two harmonics of the O−H vibration, and at λ12,000 which is a harmonic of the C−H vibration. The two O−H harmonic bands were investigated under high dispersion and a somewhat complex rotational structure was resolved. The complete interpretation of the spectrum must be postponed until the theory of the torsion oscillator rotator is further developed.

INTRODUCTION

THE authors have noticed recently that it is sometimes difficult to decide from the spectrum whether a molecule has the most symmetrical structure compatible with its constitution or whether it deviates slightly from this configuration. Small deviations from the highest possible symmetry appear to cause almost negligible splitting of vibrations which would otherwise be degenerate, and although there will be a breakdown of the transition rules which apply strictly only to the case of high symmetry the new transitions allowed may appear so weakly as to escape casual examination. In particular we have had some difficulty in deciding whether or not methyl cyanide and methyl isocyanide have a threefold axis of symmetry.

We consequently decided to study the spectrum of a molecule in some respects similar to the ones just mentioned but in which the absence of a threefold axis of symmetry is quite certain, in order to observe the effect of this lack of symmetry on the spectrum. Methyl alcohol was chosen for this purpose and in the course of its investigation some very interesting bands have been observed, of a type which has previously received little attention, namely the vibration rotation bands of a torsion oscillator. The investigation has since then very naturally developed into a systematic study of the spectra of a special class of torsion oscillators, the alcohols, the results of which will appear shortly. Since methyl alcohol is the only case so far encountered in which a rotational structure in the ordinary sense has been resolved it seemed appropriate to describe the results on this substance separately.

* This investigation is a part of a program of research made possible by a grant to one of us (R. M. B.) from the Penrose Fund of the American Philosophical Society, for which it is desired to express appreciation.

EXPERIMENTAL

The methyl alcohol vapor was confined in a glass absorption tube ten feet in length except in the high dispersion work on the band at λ7300, when a seventy-foot tube previously described[1] was used. The pressure of vapor was regulated by controlling the temperature of a side tube containing an excess of liquid, the absorption tube being kept at a somewhat higher temperature to prevent condensation. The pressures used ranged from one-quarter to three-quarters of an atmosphere though in the high dispersion work the lower pressures were found advantageous due to the pressure broadening of the lines.

In preliminary experiments the entire photographic infrared spectrum was mapped with a glass spectrograph of such dispersion that the region from the edge of the visible to the limit of sensitivity of photographic emulsions was included on one six inch plate. In the high dispersion work the first order of a 21-foot grating was employed. The plates used were the Eastman 1Z, 144Q or 144K as occasion demanded. A filter was always employed to eliminate disturbing wave-lengths as far as possible.

In the work with the glass spectrograph certain sodium, potassium and barium lines were used as wave-length standards while in the fine structure investigations with the grating the water lines were found very convenient. It was never possible to eliminate these lines entirely from the spectrum and though they caused some interference they nevertheless made very satisfactory standards. As wave-lengths of the water lines we took the values given in the 1928 revision of Rowland's table of solar wave-lengths,[2] except

[1] Badger, Bonner and Cross, J.O.S.A. **25**, 355 (1935).

[2] Revision of Rowland's Preliminary Table, Carnegie Inst. (1928).

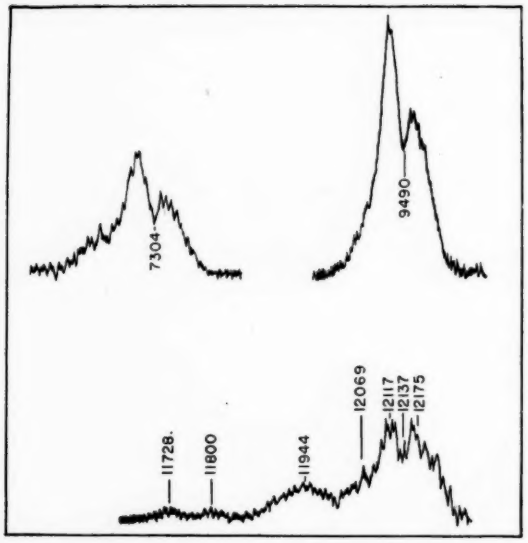

FIG. 1. Microphotometer curves of low dispersion plates of three absorption regions in methyl alcohol vapor. The curves have been corrected for a trend in plate sensitivity with wave-length.

that to the wave-lengths in the λ9500 region, given in the infrared extension of that table, we applied a correction of −0.072A to bring them into agreement with recent work of Babcock on certain of the solar lines in the farther photographic infrared.

THE LOW DISPERSION WORK

In Fig. 1 are reproduced microphotometer curves of the spectrograms taken with the glass spectrograph, which have been corrected for the trend in plate sensitivity with wave-length. These curves show certain features more clearly than those of the high dispersion plates, in particular a weak branch on the violet side of the λ7300 band, and indicate the general nature of the absorption in the harmonic of the C−H vibration at λ12,000, which we have not been able to photograph satisfactorily under high dispersion. The small maxima and minima are without significance as they are due to plate grain, but there appear to be six definite maxima in the λ12,000 region, which probably belong to at least three distinct band structures. In Table I are given the wave-lengths and frequencies of these maxima.

TABLE I. *Absorption maxima observed under low dispersion in the harmonic of the C−H vibration at λ12,000.*

λ(A)	$\nu(cm^{-1})$
11,728	8524
11,800	8472
11,944	8370
12,069	8283
12,117	8251
12,175	8211

HIGH DISPERSION WORK

We have photographed with high dispersion the bands at λ9500 and λ7300 which correspond to the transitions 0→3 and 0→4 in the O−H vibration, respectively, with results which are presented in Figs. 2 and 3, and Tables II and III. These two bands show considerable similarity of structure though there are some obvious differences. Both are rather complex and apparently consist of several branches which we have named rather arbitrarily for the sake of identification, as is shown in the figures.

At first sight both bands appear to resemble the parallel bands of methyl fluoride. There are apparently *P* and *R* branches and in the center of the band a *Q* branch, though in the λ7300 band this feature is certainly weak. However, somewhat to the long wave side of the band centers there are additional very strong lines which also resemble *Q* branches. These we have called the "*Q*'" branches. The "*P*" and "*R*" branches consist of lines which are approximately equally spaced and there is little if any convergence till one passes to the high frequency side of the maxima of the "*R*" branches. The line spacing near the centers of the bands averages about 1.75 cm^{-1} and 1.60 cm^{-1} in the λ9500 and λ7300 bands, respectively, which is very roughly what would be expected in a rotational structure in which only the large moments of inertia of the methyl alcohol molecule are involved. In the "*P*" branch of the λ9500 band there is some tendency for every third line to be more intense than the remainder. This is more evident in the plates themselves than in the microphotometer curves.

In addition to those just described each band has some additional considerably weaker branches. About 45 cm^{-1} to the violet side of the "center" of the main band there appears to be in each case a moderately strong line which we have called the "*Q*'"' branch. Still farther out there is a moderately well developed branch which in the case of the λ9500 band consists of lines with a spacing about equal to that in the "*R*" branch.

In the λ7300 region this "side band" appears more intense relative to the other branches, but no structure could be resolved in it and we have recorded the apparent maximum of absorption which may be considerably in error. These side bands we have designated by "R'."

Most of the lines of the "P" and "R" branches of the λ9500 band are fitted within experimental error by the formula:

$$\nu(\text{cm}^{-1}) = 10{,}530.7 + J(B'+B'') + J^2(B'-B'') + 4J^3C,$$

in which $(B'+B'')=1.7142$, $(B'-B'')=-0.0058$, $4C=-0.000165$ and J takes the values of the positive and negative integers. The formula fails to fit well on the extreme red side of the "P" branch. We are inclined to doubt whether the constants of the expression given have any great significance, for two reasons. In the first place a different set of constants is required to fit the λ7300 band in a similar fashion, from which it is evident that B'' cannot be interpreted as a quantity characteristic of the ground state of the molecule. Secondly, the relatively great intensity of the "R" branch, especially in the λ7300 band, gives rise to the suspicion that we may have to do with the superposition of two or more types of structure, so that the observed spacing may be of somewhat doubtful meaning.

No theory has been developed, so far as we are aware, which predicts the rotational energy levels of a molecule of the type which we find in methyl alcohol. This molecule, with little doubt, consists of a H_3CO group with a threefold axis of symmetry, and an additional hydrogen atom about 0.96A distant from the oxygen atom and so lo-

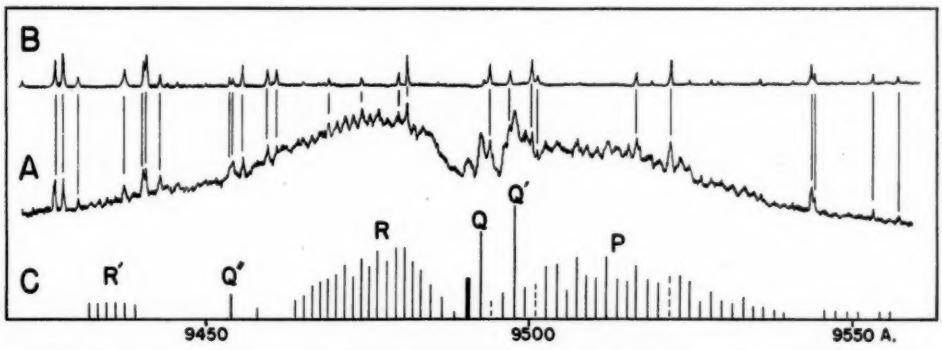

FIG. 2. The O–H harmonic band in methyl alcohol vapor at λ9500 under high dispersion. (*A*) microphotometer curve of the absorption band; (*B*) curve showing absorption of water vapor in the same region; (*C*) a representation of the maxima which were measured.

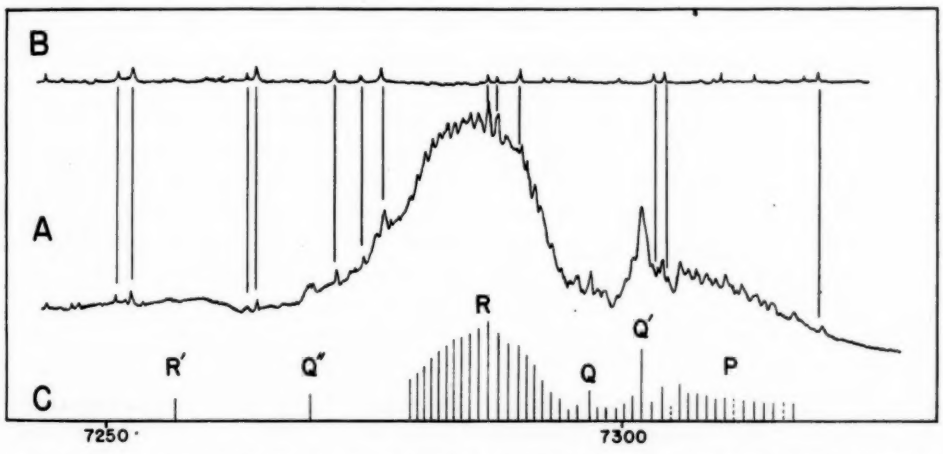

FIG. 3. The O–H harmonic band in methyl alcohol vapor at λ7300 under high dispersion. See Fig. 2 for explanation.

TABLE II. *Wave-lengths, frequencies and intensities of the lines in the λ9500 band of methyl alcohol vapor.*

Line No.	P branch			R branch		
	I	λ(A)	(cm^{-1})	I	λ(A)	(cm^{-1})
Q	10	9493.05	10531.1		—	—
1	0?	94.34*b*	529.7	5	9491.11	10533.3
2	3	96.74	527.0	?	—	—
3 Q′	20	98.14	525.5	1	88.94	535.7
4	7	99.94	523.5	3	87.27	537.6
5	?	— *b*	—	5	85.22	539.8
6	9	9503.04	520.1	8	83.91	541.3
7	9	04.78	518.1	9	82.60	542.7
8	7	06.19	516.6	11?	81.50*b*	544.0
9	10	07.78	514.8	10?	80.19*b*	545.4
10	8	09.29	513.1	9	78.60	547.2
11	8	10.91	511.4	10	77.15	548.8
12	10	12.49	509.6	9	75.88	550.2
13	8	13.95	508.0	10?	74.78*b*	551.4
14	8	15.56	506.2	9	73.32	553.1
15	9?	17.10	504.5	9	72.06	554.5
16	7	18.87	502.6	8	70.70	556.0
17	6	20.52	500.7	8?	69.43*b*	557.4
18	?	22.13*b*	499.0	7	68.31	558.7
19	7	23.69	497.2	6	66.96	560.2
20	6	25.23	495.5	5	65.71	561.6
21	4	26.82	493.8	4	64.51	562.9
22	5?	28.54*b*	491.9	}	62.77 (unres.)	
23	3	29.91	490.4	}		
24	2	31.66	488.5			
25	3	33.39	486.6			
26	2	34.95	484.8			
27	1	36.38	483.3			
28	0	38.20	481.3			
29	0	39.66	479.7			
Some additional very doubtful lines				R′ branch		
	0	9544.88	10473.9	0	9458.44	10569.7
	0	47.55	471.0	Q″ 2	54.49*b*	574.1
	0	49.46	468.9	1	39.20	591.2
	00	51.21	467.0	1	37.93*b*	592.7
	00	54.50	463.4	1	36.52	594.2
	00	56.02	461.7	1	35.26	595.6
				1.	33.90	597.2
				1	32.69	598.5

Note: for convenience we have numbered the lines in the "*P*" and "*R*" branches from the "*Q*" branch taken as arbitrary origin. Several blends with water vapor lines occur and are designated by *b*. In these cases the measurements and estimates of intensity may be in doubt.

cated that the angle between the C−O and the O−H bonds is around 105°. The hydroxyl hydrogen is presumably capable of more or less free rotation about the axis of the H_3CO group, and although three maxima of potential energy will be passed through in such a complete rotation, they are probably not very high.

Now although the methyl alcohol molecule considered as a whole is not a symmetrical rotator it deviates rather slightly from being such, the departure being due only to the light hydrogen atom which is located off the symmetry axis of the remainder of the molecule. Consequently it appeared possible that the considerations on the symmetrical torsion oscillator rotator made by Nielsen[3] might lead to a qualitative interpretation of the spectrum.

Consider first of all the case of completely free internal rotation, which our molecule may approach more or less closely. Nielsen has derived an expression for the rotational energy levels for the case in which the two portions of a molecule which are free to rotate with repect to each other have coincident symmetry axes which are at least threefold. We prefer to rewrite this expression in another form which appears to us more convenient:

$$W=(h^2/8\pi^2)\{[J(J+1)-(K_1+K_2)^2/A_x] +(K_1^2/A_z')+(K_2^2/A_z'')\}.$$

In this expression J takes the values 0, 1, 2, etc., and K_1 and K_2 the values 0, ±1, ±2, etc., subject to the restriction that $J \geqq |K_1+K_2|$; A_z' and A_z'' are the respective moments of inertia of the two separate portions of the molecule about their symmetry axes, and A_x is the moment of inertia of the molecule as a whole about an axis perpendicular to the former.

This expression was derived for a non-vibrating system, but let us extend it to the interpretation of vibration rotation bands on the assumption of little interaction between vibration and rotation. In particular let us consider some vibration which we shall regard as entirely confined to one of the two portions of the molecule which we shall assume to have a much smaller moment of inertia than the other, say $A_z' < A_z''$. It is evident that we may expect two types of band structure. In case the change in electric moment is parallel to the symmetry axes of the two rotating groups we have the selection rule $\Delta J=0, \pm 1$ and $\Delta K_1=\Delta K_2=0$, which results in a band with Q, P and R branches, the spacing in the latter two being $(h/4\pi^2 cA_x)$ cm^{-1}. This structure is similar to that of the parallel bands of methyl fluoride and may be called the "parallel type" structure.

In case the change in electric moment is perpendicular to the symmetry axes of the groups, we have as before $\Delta J=0, \pm 1$ and $\Delta K_2=0$, but $\Delta K_1=\pm 1$, which gives rise to a set of sub-bands

[3] H. H. Nielsen, Phys. Rev. **40**, 445 (1932).

the centers of which are given by the expression:

$$\nu(\text{cm}^{-1}) = \nu_0 \pm (h/8\pi^2 c)(2K_1 + 1)[(1/A_z') - (1/A_x)],$$

in which K_1 takes the values 0, 1, 2, etc. Each individual sub-band will consist of equally spaced lines with the same separation as found in the P and R branches of the "parallel type" band. Each line will really consist of a kind of Q branch with a number of other lines superposed on it. If A_z' is quite small the levels with large K_1 will be little populated, due to the Boltzmann factor, and the number of observable sub-bands might be rather small.

Now indeed the methyl alcohol bands have somewhat the appearance of a superposition of the two types of structure just described, which might perhaps be expected since the O−H vibration will produce a change in electric moment with a small component parallel to the symmetry axis of the H_3CO group and a large one perpendicular to it. We might regard the 'P', 'R' and 'R''' branches as being the three sub-bands of the perpendicular type structure corresponding to the transitions in K_1: 1→0, 0→1 and 1→2, respectively, with the P and R branches of a weaker parallel type band superposed on the first two with the Q branch lying between.

TABLE III. *Lines in the λ7300 band of methyl alcohol vapor.* (*See Table II for explanation.*)

Line No.	I	P branch λ(A)	P branch ν(cm⁻¹)	R branch I	R branch λ(A)	R branch ν(cm⁻¹)
Q	5	7296.9	13700.7	—	—	—
1	3	97.7	699.1	4	7295.7	13703.0
2	3	98.3	698.1	3	95.0	704.3
3	2	99.4	695.9	4	94.0	706.0
4	4	7300.2	694.4	6	93.2	707.6
5	5	01.0	692.9	8	92.3	709.3
6 Q'	10	01.8	691.6	11	91.7	710.5
7	3	02.7	689.8	14	90.8	712.1
8	5	03.6	688.1	16?	90.0*b*	713.6
9	?	— *b*	—	17	89.1	715.4
10	5	05.3	684.9	19?	88.1*b*	717.3
11	4	06.1	683.5	20?	87.3*b*	718.7
12	4	06.9	681.9	19	86.4	720.3
13	3	07.9	680.1	19	85.6	721.8
14	3−	08.8	678.4	18	84.9	723.2
15	4	09.8	676.5	17	83.9	725.0
16	?	—	—	17	83.4	726.0
17	3−	11.2	673.8	16	82.7	727.4
18	2+	12.4	671.6	16	82.1	728.6
19	2	13.2	670.1	15	81.3	729.9
20	2	14.0	668.5	13	80.7	731.1
21	?	—	—	9	80.0	732.4
22	1	16.1	664.8			
Q''	(apparent maximum of broad unresolved structure)					
R'					70.5	750.4
					57.7	774.7

However, this interpretation is by no means adequate. It does not take into account the multiplicity of Q branches, and we should expect the perpendicular type structure to be much more completely developed with at least a half dozen sub-bands intense enough to be observable. Certainly for a complete explanation we should have to take into account the asymmetry of the rotator and the fact that the internal rotation is not completely free. But probably even these refinements would not be sufficient, as we have been forced to conclude from our study on other alcohols. It will almost certainly be necessary to take into account a special kind of interaction between the O−H vibration and the internal rotation.

To cite a rather extreme case, it has been observed by Wulf[4] and ourselves that the harmonic bands of the O−H vibration in ortho chlor phenol each consist of two components, one strong and one weak. These have been interpreted by Pauling[5] who makes the likely assumption that the hydroxyl hydrogen is not very free to rotate and is likely to be found only in one or another of two orientations with respect to the remainder of the molecule, which correspond to potential minima. The difference in intensity of the two components is interpreted as due to the unequal depth of the two minima and the greater probability of finding the molecules in the lower energy state.

In the two orientations mentioned the frequency of the O−H vibration is considerably different and it may well be that the O−H equilibrium distance and the equilibrium angle between the C−O and O−H bonds are also affected, as well as to a lesser extent the configuration of the remainder of the molecule. In methyl alcohol the situation will no doubt be less extreme but even there the frequency of the O−H vibration will be to some extent dependent on the relative orientation of the two parts of the molecule, which will give rise to an interaction between the vibration and the internal rotation. To take these effects into account even approximately may be difficult but appears to be an interesting problem.

[4] Wulf and Liddel, J. Am. Chem. Soc. **57**, 1464 (1935).
[5] L. Pauling, J. Am. Chem. Soc. **58**, 94 (1936).

The Continuous Absorption Spectrum of Bromine: A New Interpretation

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The continuous absorption spectrum of bromine was investigated quantitatively at six temperatures from 293°K to 906°K, and the contributions of the vibrational levels $v''=0$ and $v''=1$ to the total continuum were deduced from the variation of the absorption coefficients with temperature. Contrary to expectation, the absorption from the level $v''=1$ has *three* maxima and not two, and the absorption from $v''=0$ has a decided hump on the long wave-length side of the maximum. These results can be explained if the bromine continuum is composed of two overlapping continua, the stronger one (A) with its maximum at λ4150, and the weaker (B) with its maximum at λ4950. Although it is possible to assign A to the transition $^3\Pi_{0^+u}\leftarrow{}^1\Sigma_g^+$, and B to $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$, better agreement with the Franck-Condon principle is obtained if A is assigned to $^1\Pi_u\leftarrow{}^1\Sigma_g^+$, and B to $^3\Pi_{0^+u}\leftarrow{}^1\Sigma_g^+$. The latter interpretation is also correlated with what is known of the chlorine and iodine continua. On either assumption, the value of r_e for $^3\Pi_{1u}$ of bromine is predicted to be about 2.6A.

INTRODUCTION

THE continuous absorption spectrum of bromine has already been investigated by Peskow,[1] Ribaud[2] and Gray and Style,[3] although Ribaud is the only one to have made a quantitative study of the way in which the absorption changes with temperature. Ribaud's measurements, however, were done at relatively few temperatures and wave-lengths, and since we wished to determine the contributions to the continuous absorption of the individual vibrational levels of the ground state of bromine, we have carried out measurements on the continuum at six temperatures from 293°K to 906°K, and at a number of wave-lengths. The continuous absorption of bromine extends for some thousand Angstrom units on either side of the maximum at λ4150. The band system in the visible, which reaches convergence at λ5100, is overlaid by a weak continuum which was found by Brown[4] to extend towards the red at least as far as λ6400, and it has yet to be decided definitely whether or not this is part of the main continuum. The general effect on the continuous absorption of raising the temperature of the bromine is the same as the effect that has already been observed in the case of chlorine,[5] namely a general broadening of the absorption region which is accompanied by a decrease in the absorption coefficient near the maximum; but in addition our results show that the main continuum of bromine is composed of two overlapping continua, which are due to transitions from the ground state to two different excited electronic states.

[1] N. Peskow, J. Phys. Chem. **21**, 382 (1917).
[2] G. Ribaud, Ann. de physique **12**, 107 (1919).
[3] L. Gray and D. Style, Proc. Roy. Soc. (London) A126, 603 (1929).
[4] W. G. Brown, Phys. Rev. **38**, 1179 (1931).
[5] G. E. Gibson and N. S. Bayliss, Phys. Rev. **44**, 188 (1933).

EXPERIMENTAL

We used a photographic method of obtaining the absorption coefficients that was essentially the same as the method used previously for chlorine,[5] and we shall therefore describe our technique and apparatus only in so far as they have been modified. The source of light was a 100-watt filament projection lamp, whose intensity was kept constant during runs by regulating the applied voltage. The copper gauze screens for providing calibrations of the light transmitted were themselves calibrated by means of a constant source of light, a Weston photronic cell and a galvanometer. The photronic cell-galvanometer combination was proved by means of the inverse square law to respond linearly (within 0.2 percent) to alterations in the incident intensity.

We are indebted to Professor E. J. Hartung for the loan of some bromine that had been carefully purified by distilling A. R. bromine over pure calcium bromide and calcium bromate to remove any traces of chlorine and iodine. We then subjected this sample to a fractional distillation in vacuum, during which the head and tail fractions were rejected. The bromine was introduced at about 2 cm pressure into a Hilger cell of fused silica, which had plane windows and was 5.011 cm long. In order to fill the absorption cell so that

the bromine, after purification, came in contact with nothing but silica and Pyrex glass, it was connected through an analysis bulb of 400 ml capacity to a bulb containing the liquid bromine. With the bromine immersed in liquid air, the system was thoroughly evacuated and sealed off from the line. The temperature of the liquid bromine was then adjusted so that bromine at the required pressure filled the cell and the analysis bulb, which were then sealed off. Finally, the analysis bulb was sealed off from the absorption cell, it was opened under a slightly acid solution of potassium iodide, and the liberated iodine was titrated with 0.05 N sodium thiosulphate, which had been standardised against both Merck's iodine and Merck's potassium iodate. The volume of the analysis bulb was then determined gravimetrically, and the concentration of bromine in the absorption cell was taken as equal to that in the analysis bulb.

The cell was contained in a tubular electric furnace, and its temperature was measured by chromel-alumel thermocouples. As before, a side tube projected from the furnace so that the bromine could be frozen out during the calibration exposures, and the concentration of the bromine in the cell was corrected to allow for the difference in temperature between the side tube and the furnace.

An all metal medium spectrograph by Hilger was used, with interchangeable glass and quartz optical systems. Both systems were used to cover the wave-length range, and the measurements overlapped in the region λλ4378−4144. Kodak Universal plates were used with the glass system, and Kodak Process plates with the quartz. Wave-length calibrations were obtained from an arc between brass electrodes. The lines were identified by measuring up the plate and applying the Hartmann formula to successive small regions of the spectrum, and they included some of the stronger iron lines, which were obtained by starting the arc with an iron rod. The microphotometer that was used to measure the blackening was constructed in the department. An image of the plate (which was carried on a mechanical stage) was thrown on a screen with a magnification of about fifteen. Behind a narrow slit in the screen was a Weston photronic cell that was connected to a sensitive Tinsley galvanometer. The deflections on the galvanometer scale ranged from 10 to 50 cm, and could be measured to 1 mm.

At least five plates were taken at each experimental temperature with each optical system, so that in the region where the readings with the two optical systems overlapped, there were at least ten plates at each temperature.

Judged by their internal consistency alone, our values for the fraction of the incident light transmitted by the bromine are subject to a probable error of 1 percent near the edges of the absorption, and one of about 0.7 percent near the maximum. The values recorded for wave-lengths greater than λ5100 are likely to be less precise, because of the difficulty of avoiding the bands. In addition, there are the errors in the calibration of the screens, in the determination of the bromine concentration, in the measurement of the temperature, and in the length of the absorption cell, together with any systematic errors that are inherent in the method. Of the four specific sources of error mentioned, the calibration of the screens is the most important. Because of the accuracy with which the photronic cell-galvanometer combination obeyed the inverse square law, and the consistency of the calibration values on successive days, we estimate that the transmission values of the screens were known to within 0.5 percent. It was also found that our results are subject to a small systematic error, for on comparing the overlapping results obtained with the quartz and glass optical systems, the means of the separate sets of absorption coefficients differed always in the same direction, absorption coefficients obtained with the glass system being slightly lower than those obtained using the quartz system in the spectrograph. The difference was generally about equal to the probable error of either set; but in some cases was as much as two or three times the probable error. On the whole, we believe that our results are precise to within about 2 percent; but that their accuracy may be less for the reasons just discussed.

Results

The absorption coefficient, ϵ, is defined by the relation $\log I/I_0 = -\epsilon cl$, where I_0 and I are the intensities of the incident and the transmitted light, respectively, l is the length in cm of the

TABLE I.

Wave-length A	Absorption Coefficients 20°C 293°K	127°C 400°K	258°C 531°K	384°C 657°K	494°C 767°K	632°C 906°K	Wave Number cm^{-1}
5717	13.4	18.9	19.2	23.2	27.3	27.9	17486
5495	18.4	26.5	24.8	31.4	38.2	36.8	18192
5334	29.3	40.4	36.7	37.7	53.2	44.0	18741
5153	51.0	57.9	58.4	61.1	65.2	59.3	19400
5106	63.8	64.0	62.7	66.9	68.3	68.5	19581
5017	74.8	70.0	69.1	71.6	71.6	69.8	19928
4958	81.6	77.1	74.2	76.2	76.1	74.0	20165
4919	86.0	81.4	77.8	78.8	78.2	75.6	20324
4865	90.2	86.3	83.2	82.4	81.8	78.4	20549
4811	94.4	90.8	89.8	86.8	86.6	81.4	20782
4768	98.3	94.0	93.2	90.2	89.1	82.8	20971
4722	100.7	97.0	98.2	94.3	92.8	86.7	21171
4651	105.0	102.0	102.9	99.5	97.5	89.9	21494
4587	110.3	108.0	107.7	102.6	100.3	93.8	21795
4540	113.6	112.8	111.4	107.0	103.6	95.9	22022
4480	119.0	117.5	115.3	112.0	105.3	97.6	22314
4415	127.2	122.9	119.1	113.6	108.9	99.6	22643
4378	130.6	125.9	120.3	113.4	109.8	102.3	22834
4326	139.3	130.5	123.3	114.4	111.1	103.2	23111
4275	145.3	134.5	124.9	117.5	112.8	103.6	23385
4227	150.4	136.9	126.6	117.1	113.1	103.0	23652
4178	151.5	136.1	126.2	117.4	112.8	101.3	23930
4144	151.4	137.2	125.8	115.7	111.9	102.7	24125
4063	148.0	133.8	121.2	111.4	108.0	99.2	24603
4023	142.9	128.8	117.6	108.5	105.6	96.9	24852
3969	130.4	120.0	109.8	102.9	100.0	92.5	25186
3930	119.9	112.5	103.9	97.5	94.8	88.7	25436
3862	98.6	94.7	91.1	86.5	85.7	80.4	25887
3801	75.5	77.1	78.1	75.3	76.5	72.8	26301
3735	52.8	57.0	60.8	62.6	64.4	61.3	26767
3684	38.3	43.7	48.9	51.7	52.7	53.2	27142
3640	29.3	34.2	38.6	43.3	44.9	46.8	27468
3602	19.6	26.3	33.6	37.4	38.5	41.9	27754
3528	10.5	15.5	18.0	25.4	27.5	30.8	28341
3476	6.3	10.5	12.1	18.7	20.8	24.5	28765
3441	4.3	7.8	9.2	15.8	13.4	19.7	29053
3393	2.3	4.9	5.4	10.6	11.4	12.8	29467
3338	1.0	2.9	2.9	8.5	3.9	10.0	29951
3303	1.5	1.8	2.4	6.8	—	4.1	30268
3274	1.2	—	2.0	6.8	—	—	30535

absorbing column, and c is the concentration of the gas in mole·liter^{-1}. The mean values of ϵ are given in Table I, and the values for the lowest and highest experimental temperatures are plotted against wave number in Fig. 1, which for reference also contains some values obtained by previous workers. In calculating ϵ at the higher temperatures, it was not necessary to make any correction for the dissociation of bromine, which is negligible at 630°C. Measurements that were carried out when the concentration of bromine in the cell was varied by a factor of two showed that Beer's law was obeyed within these limits. As before, we denote by ϵ_0, ϵ_1, etc. the coefficients of absorption from the vibrational levels $v''=0$, $v''=1$, etc. of the ground state, and it was shown in the previous paper[5] that ϵ, the total absoprtion coefficient at a particular wave-length and a temperature T, is related to ϵ_0, ϵ_1, etc. by the equation

$$\epsilon S_T = \sum_{v''} \epsilon_{v''} \exp\left[-(E_{v''}-E_0)/kT\right], \qquad (1)$$

where

TABLE II.

Wave Number	ϵ_0	ϵ_1	Wave Number	ϵ_0	ϵ_1
17486	2	63	23111	156	90
18192	6	81	23385	167	73
18741	14	104	23652	175	66
19400	35	117	23930	180	47
19581	69	48	24125	181	41
19928	87	19	24603	180	32
20165	94	36	24852	171	35
20324	97	48	25186	149	68
20549	101	59	25436	131	92
20782	103	70	25887	103	96
20971	106	85	26301	77	81
21171	108	91	26767	50	70
21494	110	96	27142	30	78
21795	113	116	27468	18	89
22022	116	112	27754	8	73
22314	119	131	28341	2	51
22643	130	136	28765	1	28
22834	138	110	29053	0.4	18

$$S_T = \sum_{v''} \exp\left[-(E_{v''}-E_0)/kT\right], \qquad (2)$$

$$E_{v''}-E_0 = hc[G(v'')-G(0)], \qquad (3)$$

and for the ground state of the bromine molecule[6]

$$G(v'')-G(0) = 322.1v''-1.07v''^2. \qquad (4)$$

S_T was calculated by direct summation over successive v'' levels until the contribution of higher levels became negligible, and the following values were obtained

T	293	400	531	657	767	906
S_T	1.2632	1.4661	1.7317	1.9957	2.2323	2.5327.

A slight error in the value of S_T is introduced by neglecting the effect of the rotational levels in assuming that bromine molecules in thermal equilibrium are distributed between vibrational

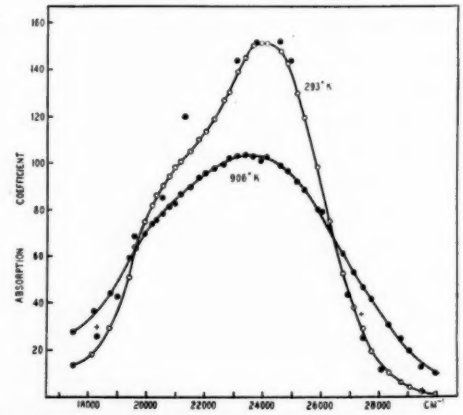

FIG. 1. The experimental absorption curve of bromine at 293°K and 906°K. Circles—our results; crosses—results of Gray and Style at room temp.; crosses in circles—results of Ribaud at room temp.

[6] W. G. Brown, Phys. Rev. **39**, 777 (1932).

levels only; but we proved that the error is less than 0.4 percent at the highest temperature by calculating one value of S_T, allowing for rotation by the method of Giauque and Overstreet.[7]

In order to obtain ϵ_0 and ϵ_1 conveniently,[7a] it is assumed that equation (1) is of the form

$$\epsilon S_T = \epsilon_0 + \epsilon_1 x + \epsilon_2 x^2 + \cdots, \qquad (5)$$

and in calculating x, 318.9 cm^{-1} was chosen as an average value of ω for the lower vibrational levels of the ground state. The experimental ϵ values were multiplied by the appropriate S_T factors, and when the values of ϵS_T for each wave-length were plotted against x, they lay on smooth curves, which were extrapolated graphically to the ordinate $x=0$ in order to obtain ϵ_0. Since all the values of x lay between 0.210 and 0.604, the extrapolation was a long one; but it was carried out independently by two observers, and the mean values are given in Table II, and are plotted against wave number in Fig. 2. Having determined ϵ_0, the value of ϵ_1, (the gradient of the ϵS_T curves at $x=0$), was found from each curve by the method of finite differences. The values of ϵ_1, which are given in Table II, and shown in Fig. 3, are undoubtedly subject to considerable errors, especially in those regions of the spectrum where ϵ_2 is relatively large.

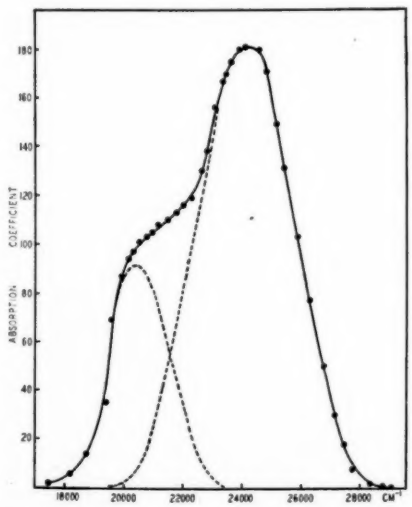

FIG. 2. The curve for absorption from the level $v''=0$ plotted against wave number. The broken lines show the resolution into two overlapping continua.

[7] W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).
[7a] Cf. Ref. 5.

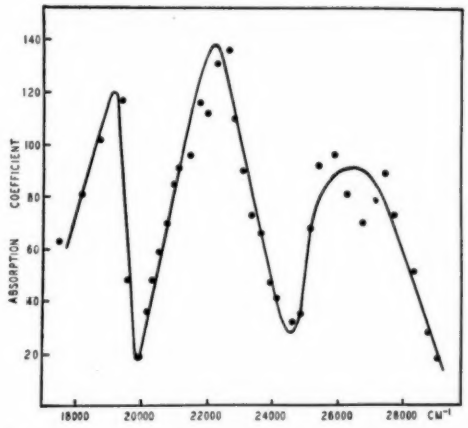

FIG. 3. The absorption from the level $v''=1$ plotted against wave number.

DISCUSSION

An interesting feature of the continuous absorption of bromine is the "hump" on the long wave-length side of the maximum of the absorption curve. Figs. 1 and 2 show that the hump becomes less obvious at higher temperatures, and that it is accentuated in the curve of the absorption from the level $v''=0$. One cannot therefore ascribe the hump to absorption from higher vibrational levels, since it becomes less evident as this absorption becomes more important. The trend of the results points strongly to the conclusion that the hump is due to the presence of a second, weaker, absorption continuum that is overlapped by the main continuum, and which must arise from transitions to a different excited electronic state. This conclusion is supported by the appearance of three maxima in the absorption from the level $v''=1$ (Fig. 3), since the theory of continuous absorption that has been developed for the case of chlorine[8] would lead one to expect two maxima if only one excited state were involved. The three maxima in Fig. 3 must be due to the superposition of the curves of two separate electronic transitions, the short wave-length maximum of one and the long wave-length maximum of the other happening to coincide fortuitously. Because of the nature of the extrapolation that gave the values of ϵ_1, we are inclined to regard the subsidiary maxima at 26,000 cm^{-1} and 27,500 cm^{-1} in the ϵ_1 curve as being due to experi-

[8] G. E. Gibson, N. S. Bayliss and O. K. Rice, Phys. Rev. **44**, 193 (1933).

mental error; but there can be no doubt that the three principal maxima at 19,000, 22,000 and 27,000 cm^{-1} are real, although our results may not give correctly the relative magnitudes of the maxima.

In order to resolve the two overlapping continua that contribute to the observed absorption, we made the assumptions, which are probably no more than a first approximation, that the stronger continuous absorption from the level $v''=0$ is symmetrically disposed about its maximum value, and that on its short wave-length side, the contribution of the weaker continuum has become negligible. The broken curves in Fig. 2 show that when this is done, the ϵ_0 curve of bromine resolves into two continua, with maxima at 24,100 cm^{-1} (A), and 20,400 cm^{-1} (B), the maximum values of the absorption coefficients being 180 and 90, respectively. The positions of these maxima coincide almost exactly with the values that have been reported for the maxima in the continuous absorption of iodine bromide.[9] Although we were confident of the purity of our bromine, we took the precaution of testing it qualitatively by a method that is capable of detecting 0.0005 percent of iodine in bromine.[10] The test was negative.

In discussing the assignment of the two continua to their respective electronic transitions, we shall consider the following states of the bromine molecule: $^1\Sigma_g^+$ (ground state), $^3\Pi_{1u}$, $^3\Pi_{0^+u}$, (involved in the visible band systems), and $^1\Pi_u$, a repulsive state predicted by Mulliken[11] to lie just above $^3\Pi_{0^+u}$. The A, or main, continuum has previously been ascribed to the $^3\Pi_{0^+u}\leftarrow{}^1\Sigma_g^+$ transition, corresponding to the principal visible band system of bromine. If this is so, our B continuum must be due to the $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$ transition, corresponding to the extreme red band system that was investigated by Brown,[4] and would then be the same as the continuous absorption that was found by Brown to blot out the visible band system when a long absorbing column of bromine was used. We compared the positions of the maxima of the A and B continua with those that are predicted by a qualitative application of the Franck-Condon principle, using Brown's data[8] for the $^3\Pi_{0^+u}$, $^3\Pi_{1u}$, and $^1\Sigma_g^+$ states of bromine to construct $U(r)$ curves according to the Morse function. The maximum of the $^3\Pi_{0^+u}\leftarrow{}^1\Sigma_g^+$ continuum is thus predicted to lie at 20,500 cm^{-1}, the observed maximum of A being at 24,100 cm^{-1}. The value of r_e for $^3\Pi_{1u}$ is not known; but if one adjusts the Morse curve for $^3\Pi_{1u}$ so that the predicted value of ν_{max} differs from the maximum of B by the same amount, the value of r_e of $^3\Pi_{1u}$ becomes 2.6A, which is considerably less than would be predicted by the usual empirical rules.

We wish, however, to suggest an alternative interpretation of the two continua, that is supported by a comparison of the data for bromine with the existent data on chlorine and iodine. Although there is no reason to suppose that the Morse function should give an exact picture of $U(r)$ at values of r very different from r_e, yet it is remarkable that the Morse curve for $^3\Pi_{0^+u}$ should predict 20,500 cm^{-1} as the value of ν_{max} of the transition $^3\Pi_{0^+u}\leftarrow{}^1\Sigma_g^+$, which coincides almost exactly with the observed maximum of our B continuum, 20,400 cm^{-1}. This tempted us to examine the consequences of assigning the B continuum to the $^3\Pi_{0^+u}\leftarrow{}^1\Sigma_g^+$ transition. The excited state of the A continuum would then be one that lies just above $^3\Pi_{0^+u}$, and would most probably be the repulsive $^1\Pi_u$ state predicted by Mulliken. The continuum associated with the $^3\Pi_{1u}\leftarrow{}^1\Sigma_g^+$ transition would then lie further to the red than our B continuum, and would overlap the visible bands—a region where we were unable to carry out accurate measurements because we had insufficient resolving power at our disposal. A consideration of the disposition of the Morse curves shows that in this case, the value of r_e for $^3\Pi_{1u}$ would still be about 2.6 A.U.

This interpretation is supported by what is known of the continuous absorption spectra of iodine and chlorine. The maximum of the iodine continuum occurs at 19,800 cm^{-1}, corresponding to our A continuum, and the low pressure data of Vogt and Koenigsberger[12] show that there is a weaker maximum at 17,900 cm^{-1} that is analogous to our B continuum. Brown[13] has reported the existence of a third region of continuous absorption in the iodine spectrum with a maximum

[9] H. Cordes and H. Sponer, Zeits. f. Physik **79**, 184 (1932).

[10] Hopkins and Williams, Ltd., *"Analar" Standards for Laboratory Chemicals* (London, 1934), p. 57.

[11] For the theory of the halogen spectra, and for previous references, see R. S. Mulliken, Phys. Rev. **46**, 549 (1934).

[12] K. Vogt and J. Koenigsberger, Zeits. f. Physik **13**, 292 (1923).

[13] W. G. Brown, Phys. Rev. **38**, 1187 (1931).

at 13,700 cm^{-1}, which he has identified with the $^3\Pi_1 \leftarrow {}^1\Sigma^+$ transition. It would then accord with our interpretation of the bromine spectrum to assign the B (subsidiary) continuum of iodine to the $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ transition, and the A (main) continuum to transitions from $^1\Sigma^+$ to the predicted $^1\Pi$ state. This assignment does not receive such good support from the Franck-Condon principle in the case of iodine as it does in the case of bromine. The Morse function predicts that the maximum of the $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ transition of iodine should occur at 19,000 cm^{-1}, which is between the experimental maxima of the A and B continua.

In the case of chlorine, the continuum with its maximum at 30,000 cm^{-1} is generally ascribed to the $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$ transition; but Mulliken[11] has already pointed out that it might possibly be due to $^1\Pi \leftarrow {}^1\Sigma^+$, since the $U(r)$ curve for the upper state that was calculated quantum-mechanically by Gibson, Bayliss and Rice[10] lies somewhat above the Morse curve for $^3\Pi_{0^+}$. If this is so, the continua that are associated with transitions to the $^3\Pi_{0^+}$ and $^3\Pi_1$ states of chlorine are yet to be discovered, and it is interesting that the absorption curve of chlorine as measured by Halban and Siedentopf[14] has two humps or subsidiary maxima in the region of very low absorption coefficients on the long wave-length side of the maximum. This region of the chlorine continuum deserves further investigation.

This interpretation helps to remove two difficulties in the theory of the halogen spectra,[13] namely the apparently too great intensity of the "intersystem" transitions $^3\Pi_{0^+} \leftarrow {}^1\Sigma^+$, and the apparent absence of $^1\Pi \leftarrow {}^1\Sigma^+$ transitions. The transitions have been estimated mainly from the intensities of the "A" continua, and if these are really due to the transition $^1\Pi \leftarrow {}^1\Sigma^+$, transitions to the $^3\Pi_{0^+}$ states are less intense than had been thought. The confirmation of our interpretation will also have a consequence that may be of interest in the photochemistry of the halogens, for since the $^1\Pi$ state dissociates into two atoms in their $^2P_{1\frac{1}{2}}$ state, the dissociation of halogen molecules by the absorption of light in the continuous region will produce mainly atoms in their ground state.

In conclusion, we would like to point out that the determination of the number of maxima in the ϵ_1 absorption curve by the method of temperature analysis affords a convenient method of deciding whether or not a given continuum is complex.

[14] H. v. Halban and K. Siedentopf, Zeits. f. physik. Chemie **103**, 71 (1922).

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The Theoretical Treatment of Chemical Reactions Produced by Ionization Processes

Part I. The Ortho-Para Hydrogen Conversion by Alpha-Particles

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The possible individual processes that may occur in a gaseous system under irradiation from alpha-particles have been examined from the theoretical standpoint. The ionization, clustering and the fate of the ions have been studied. The ortho-para hydrogen conversion under the influence of alpha-particles has been chosen as an example with which to illustrate the method of treatment. Recent experimental data by Capron have been analyzed to confirm his conclusion that atomic hydrogen is responsible for the large ratio of molecules converted to ions produced (M/N = (700 to 1000)/1). It is also shown that clustering is unimportant in this case and that the paramagnetism of the ions is of negligible importance in producing the spin-isomerization. The role of mercury atoms in removing atomic hydrogen from the system is found to be negligible. Removal of atoms by three body collision of two atoms with molecular hydrogen is slow compared with removal at the walls of the reaction vessel. Analysis of this latter process shows excellent agreement with the experimental data on the conversion efficiency of the system.

IT is well known that alpha-particles in passing through various gaseous systems expend about one-half of their energy in ionization of the molecules present and that therefore a corresponding amount of energy must be spent in excitation and dissociation of the molecules as

well as in producing translational energy. This experimental observation is in part confirmed by a theoretical calculation of Bethe[1] on the effect of alpha-particles on hydrogen atoms. His results indicate a 50 percent greater probability of excitation than for ionization. We might therefore expect in molecular systems a degree of reactivity due to excitation or dissociation independent of ionization, but there do not appear to be any experimental measurements to test this point. Such excitation of molecules may also arise during recombination of positive ions and electrons. In the absence of specific examination of effects due to such excitation,[2] we can only observe that the probability of reaction of such excited molecules should be the same as that of such species produced by photochemical excitation.

Into the details of the ionization processes under alpha-particle irradiation it is not necessary here to enter, since there is available a recent quantitative analysis of the whole ionization process as a function of sources of alpha-particles, their energy, range, ionization along a trajectory, secondary ionization and total ionization produced under given experimental conditions.[3] The positive ions formed in such processes by loss of a valence electron will have the valence properties of free radicals. As mass spectrographic evidence reveals, the primary positive ions which have lost a single electron are many times more numerous than any other and thus the discussion may, in general, be restricted to such processes. From mass spectrographic data also there are available, as appearance potentials, quantitative data on the energies required for the several ionization processes possible with a given molecule. Such data are readily available.[4]

The problem of the fate of the electron produced in the ionization process can be approached quite generally. Initially, the high speed of the electrons causes them to behave as ionizing agents, but ions so produced are included in the total number of ion pairs ascribed to the action of a given alpha-particle. When the energies of the electrons have decreased to magnitudes of the order of dissociation energies of molecules in their path, electron attachment with accompanying dissociation to form an atom or radical and a negative ion from the original molecule sometimes occur. Studies of the formation of negative ions by electron attachment by Bradbury and others[5] are of especial use in this regard. At very low velocities, it emerges from such work that only molecules which possess what are virtually free valencies, i.e., orbital angular momenta or uncoupled spin, having the power of attachment of electrons. Diatomic molecules in $^1\Sigma$ states and highly symmetrical polyatomic molecules show little or no electron affinity. The neutralization process whereby the electron disappears is discussed subsequently; consideration will also be given to the negative ion as a clustering center.

With respect to the positive ion fragment from the ionization process there are several possibilities. The ion may react with another molecule to form a new type of ion. It may also interact with such a molecule to exchange electrons in the collision process. This event needs especial examination in the case of spin-isomerization to be considered. The ion may act as a clustering centre for one or more neutral molecules attached to the ion by virtue of their polarization in the ion field. Finally, the neutralization process of the ion with one or other of the negatively charged species present together with the chemical consequences of such neutralization forms the concluding event in the processes immediately following ionization. These several alternatives will now be examined specifically in the one-component system which the ortho-para hydrogen mixture forms. This represents an especially favorable starting point since much is now known from the theoretical and practical standpoint concerning the ions and molecules involved.[6]

[1] Mott and Massey, *Theory of Atomic Collisions* (Oxford Press, 1933) pp. 185, 224; Bethe, Ann. der Physik **5**, 325 (1930); Blackett, Proc. Roy. Soc. **A135**, 132 (1932).

[2] The possibility of such effects was first emphasized by Wourzel, J. de Phys. et le Rad. **6**, 77 (1920).

[3] W. Mund, *L'Action Chimique des Rayons Alpha* (Hermann et Cie., Paris, 1935).

[4] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931); H. Sponer, *Molekulspektren*, Vols. I and II (Julius Springer, 1935 and 1936).

[5] N. E. Bradbury, Phys. Rev. **44**, 883 (1933); J. Chem. Phys. **2**, 827, 840 (1934); N. E Bradbury and H. E. Tatel, J. Chem. Phys. **2**, 835 (1934); F. Block and N. E. Bradbury, Phys. Rev. **48**, 689 (1935); L. B. Loeb, Phys. Rev. **48**, 684 (1935).

[6] Condon and Smyth, Proc. Nat. Acad. **14**, 871 (1928). E. Condon, Phys. Rev. **35**, 658 (1930). H. D. Smyth, Proc. Roy. Soc. **A102**, 283 (1922); Phys. Rev. **4**, 452 (1925); Rev. Mod. Phys. **3**, 347 (1931). W. Bleakney, Phys. Rev. **35**, 1180 (1930); **40**, 496 (1932). Brasefield, Phys. Rev. **31**,

The Ionization Process

The products of ionization of hydrogen by alpha-particles have never been made the object of particular study. All that is definitely known is the number of ion pairs produced per alpha-particle and from this it is calculated that each ion consumes 33.0 electron-volts or about 100 percent more than the amount, 15.37 volts, necessary to produce the molecule ion, H_2^+. The products of ionization by electrons of controlled speeds have been very thoroughly investigated, with the aid of mass spectrographic methods.[7] From this it is known that up to speeds of 500 ev more than 90 percent of the primary products are the molecule ion, H_2^+, which first appears at 15.37 volts. At about 18 volts, H^+, appears weakly, while fast H^+ ions are produced at 26 and again at 30 volts. These also are weak compared with H_2^+. At 15.9 volts, especially at high pressures, there is a plentiful production of H_3^+ ions as a secondary effect, while, if the ion has some kinetic energy, the ion H^+ also appears in quantity at high pressures. Such products may be attributed to secondary collisions described by the equations

$$H_2^+ + H_2 = H_3^+ + H, \qquad (1a)$$

$$H_2^+ + H_2 = H^+ + H + H_2. \qquad (1b)$$

The latter reaction requires an activation energy of at least 2.639 ev. With electron speeds from 11.5 to 15 volts there is definite evidence of atomic dissociation presumably by excitation of the molecule to the $^3\Sigma$ state which subsequently dissociates into two H atoms. This effect is described by Smyth as "fairly strong."

It is evident that, at the relatively high pressures obtaining in alpha-particle work, all such ionization processes may occur along the track of the particle. Since, in such case, it is the singly-charged ions which predominate, we reason by analogy that the preponderant ion primarily produced by the alpha-particle is H_2^+ and that this may represent upwards of 90 percent of the total primary ionization. The excess energy consumed but not in ionization may in large part have gone into the production of $^3\Sigma$ molecules which immediately dissociate. Each pair of atoms thus formed would account for 12 volts.[8] On this basis one might expect approximately equal amounts of (2H) and H_2^+ from the excitation and ionization processes respectively. The possible secondary processes will now be examined.

52 (1928). Hogness and Lunn, Proc. Nat. Acad. **10**, 398 (1924); Phys. Rev. **26**, 44 (1925). W. Lozier, Phys. Rev. **36**, 1417 (1930); **44**, 575 (1933). Dorsch and Kallmann, Zeits. f. Physik **53**, 80 (1929). Hughes and Skellett, Phys. Rev. **30**, 11 (1927). Dempster, Phil. Mag. **31**, 438 (1916); **3**, 115 (1927).

[7] Smyth, reference 4: Bleakney, Phys. Rev. **35**, 1180 (1930).

[8] Coolidge, James and Present, J. Chem. Phys. **4**, 187 (1936); W. Finkelnberg and W. Weizel, Zeits. f. Physik **68**, 577 (1931); N. D. Smith, Phys. Rev. **49**, 345 (1936).

The Formation of H_3^+ by Secondary Collision

The separation, d, between the centers of gravity of H_2 and of H_2^+ at the activated state is so large, because of the nature of their interaction energy, that each of the molecules may be assumed to rotate as freely as they do when they are far apart.

It is known that the interaction of a hydrogen atom with a hydrogen molecule requires about 7 kcal. of activation energy.[9] The activation energy of $H_2+H_2^+$ is probably small compared to this value since, at large distances, the molecule is attracted by ion-polarization forces to the ion and this attraction may persist to small distances. If it does so, an apparent activation will still arise from the rotational energy of the system as a whole. For a system rotating with a quantized angular momentum, $jh/2\pi$ the energy is increased, by the centrifugal forces, to an amount $E_{\text{rot}} = j(j+1)h^2/8\pi^2 m_{\text{H}} d^2$.[10] Since the ion polarization energy is $E_{\text{pol}} = -\alpha e^2/2d^4$, these two potentials superposed give an activation energy and an activated state for every value of j different from $j=0$. The quantity α is the polarizability of the hydrogen molecule. Following Eyring,[11] we obtain

[9] A. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930); Geib and Harteck, ibid., Bodenstein Festband, 849 (1931).

[10] In this paper m with an appropriate subscript indicates the mass of the atom or molecule in grams, while M is the mass in atomic weight units.

[11] Eyring, J. Chem. Phys. **3**, 107 (1935); Eyring, Gershinowitz and Sun, J. Phys. Chem. **3**, 786 (1935).

for the rate of reaction

$$k=\frac{\kappa(2\pi m_{H_4}kT)^{\frac{3}{2}}h^{-3}[1+\sum_{J=1}^{\infty}(2J+1)\exp-(E_{rot}^*-E_{pol}^*)(kT)^{-1}]kTh^{-1}}{(2\pi m_{H_2}kT)^{\frac{3}{2}}h^{-3}(2\pi m_{H_2^+}kT)^{\frac{3}{2}}h^{-3}}.$$

In this expression, the rotational and vibration partition functions for H_2 and H_2^+ have already been cancelled in the numerator and denominator. The starred energy symbols refer to the respective energies at the activated state, for which state the expression, $j(j+1)h^2/8\pi^2m_Hd^2-\alpha e^2/2d^4$, has a maximum value. Hence, the distance, d^*, has the value,

$$d^*=(j(j+1)h^2/8\pi^2m_H\alpha e^2)^{-\frac{1}{4}}, \tag{5}$$

and at this distance the activation energy becomes

$$E_{rot}^*-E_{pol}^*=j^2(j+1)^2h^4/128\pi^4m_H^2\alpha e^2. \tag{6}$$

Setting $a^2=h^4/128\pi^4m_H^2\alpha e^2kT$ we can write the quantity A inside the square brackets in the velocity equation as

$$A=1+\sum_{j=1}^{\infty}(2j+1)\exp-j^2(j+1)^2a^2. \tag{7a}$$

Since the numerical value of a^2 is small, $2.74\times10^{-3}T^{-1}$, the summation, A, may be replaced by the integral

$$A=\int_0^{\infty}(2j+1)\exp-j^2(j+1)^2a^2dj=\int_0^{\infty}(1/a)\exp(-y^2)dy=\sqrt{\pi}/2a=(\pi^{\frac{1}{2}}/2)(2\alpha kT)^{\frac{1}{2}}8\pi^2m_He^{\frac{1}{2}}h^{-2}. \tag{7b}$$

Hence, our expression for the velocity of reaction becomes:

$$k=\kappa\left(\frac{m_{H_4}}{m_{H_2}m_{H_2^+}}\right)^{\frac{3}{2}}\frac{kT}{h}\cdot\frac{h^3}{(2\pi kT)^{\frac{3}{2}}}\cdot\frac{2\pi^2m_{H_2}e}{h^2}(2\pi kT)^{\frac{1}{2}}$$

or $k=\kappa2\pi m_H^{\frac{1}{2}}e\alpha^{\frac{1}{2}}=2.069\times10^{-9}\kappa$ cc per molecule per sec. or 1.25×10^{15} cc per mole per sec. It is evident that the velocity of this reaction is very high even when the possible rotation of the system is taken into account.

The Formation of H^+ by Secondary Collision

In this reaction the process must be expressed by the equation, $H_2+H_2^+=H_2+H+H^+$ which consumes 60.9 calories of energy.[12] It occurs therefore only on collisions between molecules and ions in which the relative kinetic energy of impact is in excess of 60.9 kcal. It must therefore be a process of small probability with ions produced by electrons with velocities close to the ionization potential. The mass spectrographic data agree with this conclusion since H^+ is first produced in quantity at about 18 volts ±0.3; the secondary production requires that the impact contribute the necessary kinetic energy. It is also known that H^+ ion tends to disappear in presence of hydrogen molecules to produce H_3^+ presumably by a three body collision involving H^++H_2. This fact therefore renders the case of the H^+ ion less important also in alpha-particle systems and enhances the relative importance of H_3^+ ion.

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[12] O. Burrau, Det. Kgl. Danske Vid. Selskab **7**, 1 (1927); E. A. Hylleraas, Zeits. f. Physik **71**, 739 (1931); G. Jaffe, ibid. **87**, 535 (1934).

The Formation of Clusters

The general problem of clustering around ionic species may be formulated in terms of the equilibrium $A+B^+ \rightleftarrows A\cdot B^+$, for which we may write the equilibrium constant K in terms of the partition functions, F, for the several species as follows:

$$K=(F_{AB^+}/F_A\cdot F_{B^+})\exp -E_0/kT. \tag{9}$$

If d represents the distance between ion B^+ and clustering molecule A, then $E_0=-\alpha e^2/2d^4$. The partition function for the cluster is

$$F_{AB^+}=F_{\mathrm{rot}_A}F_{\mathrm{vib}_A}F_{\mathrm{rot}_B}F_{\mathrm{vib}_B}\frac{8\pi^2 I_{A\cdot B^+}\cdot kT}{h^2}\left(2\sinh\frac{h\nu_{A\cdot B^+}}{2kT}\right)^{-1}\frac{(2\pi m_{A\cdot B^+}kT)^{\frac{1}{2}}}{h^3}.$$

Here, $I_{A\cdot B^+}=d^2(m_Am_B)/(m_A+m_B)$. From this we deduce that

$$K=\left(\frac{M_A+M_B}{M_AM_B}\right)^{\frac{1}{2}}d^2\frac{(h^2N/2\pi kT)^{\frac{1}{2}}(8\pi^2kT/Nh^2)\cdot 10^{16}}{2\sinh h\nu_{A\cdot B^+}/2kT}\exp \alpha e^2/2d^4$$

$$=6.302\times10^{-24}\left(\frac{M_A+M_B}{M_AM_B}\right)^{\frac{1}{2}}\frac{d^2\exp 277a/d^4}{\sinh h\nu_{A\cdot B^+}/2kT}\ \text{molecules per cc.} \tag{10}$$

In this expression, $a=(\alpha+\mu^2/3kT)\times10^{-24}$ cm^3 where α = the polarizability of the molecule A and μ = the electric moment of molecule A. In the corresponding expression for K in moles per cc the numerical coefficient is 3.822.

For the frequency $\nu_{A\cdot B^+}$ we assume a value 100 cm^{-1} or a value for $h\nu_{A\cdot B}=0.284$ kcal. The value of $\sinh h\nu_{A\cdot B^+}/2kT$ becomes for $T=300°$, $\sinh 0.238=0.240253$. Including this in the numerical coefficient we obtain

$$K=15.908\left(\frac{M_A+M_B}{M_AM_B}\right)^{\frac{1}{2}}d^2\exp 277a/d^4\ \text{moles per cc.} \tag{11}$$

The molecular concentration $[A]$ when the partial pressure, P_A, of the species is expressed in atmospheres, for a temperature of 300° Abs., is $[A]=4.0600\times10^{-5}P_A$. We can therefore express the ratio of concentrations of clustered ions to free ions quite generally by the expression

$$\frac{[A\cdot B^+]}{[B^+]}=6.46\times10^{-4}\left(\frac{M_A+M_B}{M_AM_B}\right)^{\frac{1}{2}}d^2P_A\exp 277a/d^4, \tag{12}$$

the distance d being expressed in A units, the polarizability a in 10^{-24} cm.^{3} Applying this equation to several types of clusters possible in the $H_2-H_2^+-H_3^+$ system we obtain the following data:

(i) $H_2+H_2^+$: $d=2.8$A; $a=0.8$; $P_A=1$ atm.;

$$[H_2\cdot H_2^+]/[H_2^+]=6.46\times10^{-4}\times(2.8)^2\exp 3.605=0.186;$$

(ii) $H+H_3^+$: $d=2.8$A; $a=0.663$; $P_A=1$ atm.; $[H\cdot H_3^+]/[H_3^+]=0.116$;

(iii) $H_2+H_3^+$: $d=2.8$A; $a=0.8$; $P_A=1$; $[H_2\cdot H_3^+]/[H_3^+]=0.173$.

We see, therefore, that, in hydrogen, approximately one ion in 5 to 9 will be present associated with one molecule; the probability of two molecules being associated falls to values of the order of one in 25 to 81.

The Formation of Negative Ions

It is known from the data of Hylleraas[13] that the electron affinity of hydrogen atom is 16.48 kcal., so that H^- ions will be formed by interaction of electron with atomic hydrogen in the presence of a third body to dissipate excess energy as kinetic energy.

The formation of H_2^- ions may be examined by the method already employed by Pauling[14] for the treatment of the interaction of $He+He^+$ to form He_2^+. The only difference in the two problems is that for H_2^- the nuclear charges are unity while they are two for the He_2^+ case. Using the $1s$ hydrogen-like eigenfunctions $a_1=(Z^3/\pi)^{\frac{1}{2}}e^{-Zr_{a_1}}$, $b_1=(Z^3/\pi)^{\frac{1}{2}}e^{-Zr_{b_1}}$, where Z is a screening constant and r_{a_1} and r_{b_1} are the distances of electron (1) from nuclei a and b respectively, the eigenfunction which corresponds to the lowest energy state is:

$$\Psi=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} a_1\alpha_1 & b_1\beta_1 & b_1\alpha_1 \\ a_2\alpha_2 & b_2\beta_2 & b_2\alpha_2 \\ a_3\alpha_3 & b_3\beta_3 & b_3\alpha_3 \end{vmatrix}+\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} a_1\beta_1 & b_1\alpha_1 & a_1\alpha_1 \\ a_2\beta_2 & b_2\alpha_2 & a_2\alpha_2 \\ a_3\beta_3 & b_3\alpha_3 & a_3\alpha_3 \end{vmatrix}.$$

Here α and β are spin functions of the electron corresponding to $S_Z=+\frac{1}{2}(h/2\pi)$ and $-\frac{1}{2}(h/2\pi)$ respectively. The corresponding energy of the system is found to be:

$$E=\frac{e^2}{a_0}Z\left\{-\frac{3}{2}+\frac{1}{R}+\frac{1}{N}[-(3+2I-I^2)G-(1-2I-3I^2)J+L(aa,aa)+2(1-I)L(aa,ab)\right.$$
$$\left.+(2+I)L(aa,bb)-(1+3I)L(ab,ab)]+\frac{1}{2}\frac{(Z-1)}{N}[3+I+I^2+3I^3+2(1-2I-3I^2)J]\right\},$$

where $N=(1+I-I^2-I^3)$ and the integrals

$$I=\exp-\rho\left(\frac{\rho^2}{3}+\rho+1\right)=\frac{1}{\pi}\int\exp-(\rho_a+\rho_b)d\tau,\quad G=\frac{1}{\pi}\int\rho_b^{-1}\exp-2\rho_a d\tau,$$

$$J=\frac{1}{\pi}\int\rho_a^{-1}\exp-(\rho_a+\rho_b)d\tau,\quad L(aa,bb)=\pi^{-2}\int\int\rho_{12}^{-1}\exp-2(\rho_a+\rho_b)d\tau_1 d\tau_2,\quad \text{etc.}$$

In these integrals, the screening constant Z times the separation, R, between the points a and b is $\rho=ZR$ and $\rho_{12}=Zr_{12}$, where r_{12} is the distance between electrons 1 and 2. These integrals have been treated in the literature.[15] For a particular value of the internuclear separation, Ra_0, the screening constant Z is varied so as to make E a minimum. We obtain a minimum energy for $R_{ab}=1.8$A. Here $E=2E_H+16.5$ kcal., i.e., an electron is repelled from H_2 even at the most favorable internuclear separation. However, a better calculation would lead to an electron repulsion for H^- of 16.48 kcal. instead of the 37.36 kcal. of electron separation which our calculation leads to. We assume, as did Pauling in the He_2^+ case, that this type of calculation is in error by the same amount for all nuclear configurations. With this assumption, Pauling obtained excellent agreement with the experimental values for He_2^+. For this reason, we subtract (16.48+37.36) kcal. from all of our calculated energies. We now obtain a minimum energy of -37.4 kcal. at $Ra_0=1.8$A. This energy of H_2^- is plotted in Fig. 1. It is seen that there actually exist stable states for H_2^-. The zero point energy is about one kcal. However, from Fig. 1, it is evident that if an electron collides with H_2 in accord with the Franck-Condon principle, it must possess an energy of around the energy of dissociation of H_2 before it can form H_2^-. But this H_2^- possesses more vibra-

[13] Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[14] Pauling, J. Chem. Phys. **1**, 56 (1933).
[15] Hirschfelder, Eyring and Rosen, J. Chem. Phys. **4**, 121 (1936).

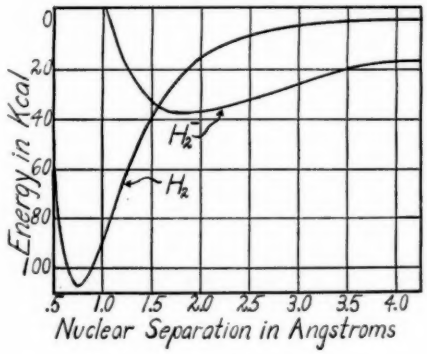

FIG. 1. Potential energy curves of H_2 and H_2^-.

tional energy than is required to dissociate into $H+H^-$ and therefore H_2^- could not be formed in this manner. If an H atom collides with H^-, it has more than enough energy to reach that part of the potential curve in which $H_2+\epsilon$ is more stable than H_2^-. We, therefore, conclude that, (1) H^- can be formed by a three body collision between H, ϵ, and another atom or molecule, without any activation energy. H^- may also be formed by a collision of an electron with H_2 with an activation energy of about 4 to 6 ev (2) H_2^- stable states exist but they cannot be reached by electron collision with H_2. They might be formed by unusually favorable three body collisions between H, H^-, and a third atom or molecule. The probability for this ion to be formed is so low that it is not surprising that it has never been experimentally observed.

THE NEUTRALIZATION PROCESS

The process $A^+ + B^- \rightarrow A + B$ has been observed experimentally and calculated theoretically[16] to have a specific reaction rate constant, expressed in cc per molecule per second, of $\alpha \approx 10^{-6}$, if the gas is air. For most other gases experiments give values of about this same magnitude. It is not ordinarily very specific since most gases contain sufficient impurity to combine to form the negative ions. However, in the case of unusually pure argon values as low as $\alpha = 10^{-10}$ have been observed by Kenty.[17]

[16] E. B. Loeb and L. C. Marshall, J. Frank. Inst. **208**, 372 (1929); Thirkill, Proc. Roy. Soc. **A88**, 477 (1913); Harper, Cambridge Phil. Soc. Proc. **28**, 219 (1932); Eriksen, Phil. Mag. **18**, 328 (1909).

[17] Kenty, Phys. Rev. **32**, 624 (1928).

A value of α as low as 10^{-10} probably indicates that neutralization involves a third body in addition to the electron and positive ion while a value of 10^{-6} would then indicate that no third body is necessary, the neutralization involving only a negative and positive ion.

The process of free electron capture necessarily involves three bodies, i.e., two molecules and an electron unless the resultant molecule dissociates. The third body is required to carry away enough energy to stabilize the electron-positive ion complex. If an electron is attached to a molecule to form a negative ion it may leak to a positive ion upon their near approach without having sufficient energy to escape subsequently into empty space. A stabilization collision in this case is unnecessary so that the process appears bimolecular. At atmospheric pressures such a mechanism is favored over a trimolecular one. If the molecule cannot form a negative ion then it can only stabilize the system, positive ion plus electron, if it is within a kinetic theory diameter of the positive ion when the latter is struck by the electron. Such three body collisions are much less frequent than the above type of bimolecular collision at atmospheric pressure. This would account for the slow rate in pure argon. That the third body must be in the neighborhood of the positive ion rather than the electron unless there are inelastic collisions can be seen as follows. As a consequence of the law of conservation of energy and momentum, an electron can only lose the fraction of its energy $4m_e/m_{\text{atom}}$ in an elastic collision with an atom or molecule. To permit electron capture in this way the energy transferred must be of the order of kT. But since, in the neutralization process, the kinetic energy of the electron cannot be more than a small fraction of the ionization potential at points accessible to a third body any direct transfer of energy from the electron to the third body is negligible. This same argument applied to conservation of angular momentum excludes the possibility of the electron transferring energy to the rotational states of the molecules. The excitation of higher vibrational or electronic states of the neutral molecule is improbable but not excluded.

The electron-positive ion system is, of course, a very excited state of the molecule which is

being formed. This excited state may dissociate, or give the energy to other molecules. Radiation processes are of low probability compared to collision processes for taking up the excess energy and so can be ignored.

Recombination of H_3^++Electron

When H_3^+ is neutralized, the resulting H_3 surely dissociates since it is unstable. Initially, the H_3^+ is in a singlet state. When the electron is coupled to the spin of the molecule, the total spin of the system must correspond to a doublet. Whatever electronic orbitals are involved one state, (1), of the doublet, i.e., energetically the lowest, corresponds to a binding between two of the three nuclei and this state dissociates to give H_2+H. The other state, (2), of the doublet corresponds to a repulsion between all three atoms and hence a dissociation into three H atoms. The expression for the energy in which the spin has been properly considered and the approximations consist in neglecting certain orthogonality and multiple exchange terms are:[18]

$$E_1=A+B+C-(\tfrac{1}{2}((\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2))^{\frac{1}{2}}, \quad (13a)$$

$$E_2=A+B+C+(\tfrac{1}{2}((\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2))^{\frac{1}{2}}, \quad (13b)$$

and the occurrence of either is equally probable. The Greek letters correspond to the three single exchange bonds and Latin letters to the additive part, these states occur in pairs with equal probability of either occurrence, one yielding 3 hydrogen atoms, the other one atom and one molecule. Since the resulting molecule will be energy rich, it may dissociate on subsequent collision. The average yield from this neutralization process will therefore be more than two H atoms and less than 3 H atoms.

Recombination of H_2^++Electron

If the H_2^+ reacts with H_2 with the specific reaction rate of 10^{15} cc per mole per sec. (as seems probable) the H_2^+ has only a fleeting existence at atmospheric pressure of H_2. However, we may easily show what recombination processes take place between H_2^+ and an electron.

[18] London, *Probleme der Moderne Physik*, edited by Debye (Hirzel 1928) p. 104.

H_2^+ is initially a doublet state. When the electron is coupled to the spin of the H_2^+ the total system will be either a singlet or a triplet with relative probabilities of 1 and of 3, respectively. The singlet states of H_2 are stable (excited or unexcited states) while the triplet states are all repulsive and correspond to the dissociation into two hydrogen atoms. The dissociation process is bimolecular while the capture to form the singlet state requires the presence of a third body and therefore does not occur as frequently. Often the singlet state will only result in excitation without the subsequent production of H atoms. The atom yield due to the triplet states will be $\frac{3}{4}\times 2$ and that due to the singlet state will be somewhat less than $\frac{1}{4}\times 2$, the total being between 1.5 and 2.0 H atoms.

We do not consider the neutralization processes involving H_3^++H^- owing to the relatively low concentration of the latter species and since analysis shows that the atom yield cannot thereby be materially changed.

The general conclusion from the consideration of these neutralization processes is therefore that, the overwhelming majority of the neutralizations will involve H_3^+ and produce 2 to 3 H atoms. Those processes involving H_2^+ produce 2 H atoms as a maximum and in general yield between 1.5 and 2 H atoms per neutralization. Since in the formation of H_3^+, one H atom is already formed it is evident that the total net yield of atomic hydrogen will at least be from 3 to 4 H atoms per ion pair produced. Further, to the extent that the excitation processes occurring in the track of the alpha-particle may produce additional atomic hydrogen these minimum yields will be exceeded. Empirical evidence from our analysis of recent data by Lind and Livingston[19] on the alpha-particle reaction of hydrogen and bromine indicates that the *total* yield from ionization and excitation may reach 6 H atoms measured in terms of ion-pairs produced.

The Ortho-Para Conversion

There remains for analysis the several effects of alpha particle, ions, ion-exchange and atomic hydrogen on the conversion of para to ortho

[19] Lind and Livingston, J. Am. Chem. Soc. 58, 612 (1936). This work will be considered in detail in a later paper.

hydrogen at room temperatures as studied experimentally by Capron.[20]

1. Direct conversion by alpha particle

An alpha particle passes through the gaseous mixtures with velocities of the order of 10^9 cm per sec. Such a rapidly moving charged particle has associated with it a magnetic field as measured at the center of an H_2 molecule of

$$H=\frac{v}{c}\frac{2ea_s}{r^3(1-v^2/c^2)^{\frac{1}{2}}}.$$

Here r and a_s are the actual separation and the distance of closest approach of the alpha particle to the H_2 molecule. The velocity of the alpha particle, v, is always small enough with respect to the velocity of light, c, that we may neglect the difference between $(1-v^2/c^2)^{\frac{1}{2}}$ and unity. This field is identical with the field which Wigner[21] considered for the case of ortho-para conversion by paramagnetic molecules. Here we must let $\mu_a=2ea_sv/c$, to use Wigner's terminology. Only the inhomogeneous part of the field is effective in producing spin-isomerism. This produces a coupling or uncoupling of the nuclear spins which is measured by the matrix components connecting the ortho with the para states. Realizing that the effect is very small, the eigenfunction for the molecule may be expanded in terms of the unperturbed rotational eigenfunctions and the coefficients evaluated by a standard perturbation method. The collision process is idealized in a manner suggested by the work of Kallmann and London,[22] i.e., the magnetic field is turned on with its greatest intensity for a length of time, $t=a_s/3v$. This method of Wigner gives a rough average of the effect and is better the shorter the time for the collision. Following Wigner we obtain for the probability of a transfer from the zero rotational level to the first

$$W=\frac{4}{3}\frac{a^2_{H_2}\mu_p^2e^2}{(h/2\pi)^2c^2a_s^4}=\frac{2.66\times10^{-48}}{a_s^4}. \quad (15)$$

W is only 2.66×10^{-16} if $a_s=1$A and has decreased to 10^{-18} when $a_s=4$A. We can calculate an upper limit for the number of molecules M which each alpha particle converts,

$$M_\alpha=R\rho\int_0^\infty W2\pi r dr. \quad (16a)$$

Here R=range of the alpha particles, ρ=density of molecules in the gas. When r is less than some value, x, we assume that the molecules will certainly be converted and for r greater than x we use the value of W defined in the Eq. (15). Such an assumption leads to too large a value of M_α regardless of what value of x is chosen. Therefore

$$M_\alpha<\rho R\int_0^x 2\pi r dr+R\rho(2\pi)2.66\cdot10^{-48}\int_x^\infty\frac{dr}{r^3}, \quad (16b)$$

$$M_\alpha<2\pi R\rho(x^2/2+2.66\times10^{-48}/4x^4).$$

This expression is least when $x=(2.66\times10^{-48})^{1/6}$. Hence,

$$M_\alpha<6.53\times10^{-16}R\rho. \quad (16c)$$

For atmospheric pressure, in H_2 gas, $R=18.4$ cm ($T=15$°C; radon) and $\rho=2.6\times10^{19}$ cm^{-3}. Hence, $M_\alpha<3.1\times10^5$. But the number of ion pairs formed by each α particle, N, is

$$N=2.2\times10^5;$$
$$\therefore\quad M_\alpha/N=1.5 \text{ as an upper limit.} \quad (17)$$

This is negligible in comparison with the experimentally observed value of $M/N\approx1000$.

2. Ortho-para conversion by H_2^+, H_3^+ and H

If H_2^+ had a mean lifetime of a few collisions instead of the fleeting existence which we have already indicated in the preceding discussion, it might be supposed that, in collisions, an electron could be transferred from H_2 molecules to H_2^+ and this chain process would be efficient in converting para to ortho hydrogen.

$$H_2^+ + H_2 \rightarrow H_2 + H_2^+. \quad (b)$$

Because the positive ion is of the same species as the molecule, this electron exchange is more efficient than electron exchanges between unlike ions and molecules. In the earlier experimental work on electron exchange it was thought that such a transfer would occur on a large fraction

[20] Capron, Ann. Soc. Sci. Bruxelles, **55**, 222 (1935).
[21] E. Wigner, Zeits. f. physik. Chemie **B23**, 28 (1933).
[22] H. Kallmann and F. London, Zeits. f. physik. Chemie **B2**, 207 (1929).

of the collisions. More recent work of Wolf[23] indicates that this exchange may require an activation energy of the order of the ionization potential of H_2. However, we shall prove that no spin isomerization takes place in H_2^+ except during collisions or at the same time that electron jumps occur. The efficiency of the H_2^+ for spin isomerization during collisions without electron transfer is similar in magnitude to that of other paramagnetic molecules. H_2^+, therefore, cannot contribute materially to the spin isomerization. The following is the proof that no spin isomerization occurs except during collision. The energy of coupling of the electron spin, $\mathbf{S}_\epsilon$, with the nuclear spins, $\mathbf{S}_1$ and $\mathbf{S}_2$, in H_2^+ is:

$$Q=-\mu_p\mu_\epsilon\left[\frac{\mathbf{S}_\epsilon\cdot\mathbf{S}_1}{r_1^3}+\frac{\mathbf{S}_\epsilon\cdot\mathbf{S}_2}{r_2^3}\right]. \tag{18}$$

Only the part of the energy which is antisymmetric with respect to the nuclei may contribute to the spin isomerization. The H_2^+ (para) state is:

$$\Psi_{\text{para}}=\alpha_\epsilon(\alpha_1\beta_2-\alpha_2\beta_1)\psi_\epsilon(x_\epsilon-x_1,\ x_\epsilon-x_2)\times\chi_0(x_1,\ x_2). \tag{19}$$

Here α and β are the spin eigenfunctions of the electron ϵ, and nuclei 1, and 2. $\Psi_\epsilon(x_\epsilon-x_1,\ x_\epsilon-x_2)$ is the electronic eigenfunction of the molecule and $\chi_0(x_1,\ x_2)$ is the nuclear eigenfunction. Ψ_ϵ, as the notation indicates, is a function of the six components of the distance between the electron and the two nuclei, and χ_0 is a function of the nuclear coordinates only. The subscript on χ indicates the rotational quantum number of the molecule as a whole. Operating on Ψ_{para} by the operator Q, we obtain:

$$Q\Psi_{\text{para}}=\left(\frac{h}{2\pi}\right)^2\tfrac{1}{2}\mu_p\mu_\epsilon(r_1^{-3}-r_2^{-3})\times[\Psi_{\text{para}}-\beta_\epsilon\alpha_1\alpha_2\psi_\epsilon\chi_0]. \tag{20}$$

As far as spin considerations go, the $\beta_\epsilon\alpha_1\alpha_2\psi_\epsilon\chi_0$ will combine with the ortho H_2^+ eigenfunction: $\Psi_{\text{ortho}}=\beta_\epsilon\alpha_1\alpha_2\psi_\epsilon'\chi_1$. The matrix element for this interaction is:

$$\Sigma\int\bar{\Psi}_{\text{ortho}}Q\Psi_{\text{para}}d\tau=\tfrac{1}{2}\mu_p\mu_\epsilon\int\chi_0\bar{\chi}_1d\tau_1d\tau_2\int\overline{\psi_\epsilon'}\times(r_1^{-3}-r_2^{-3})\psi_\epsilon d\tau_\epsilon. \tag{21}$$

[23] Franz Wolf, Zeits. f. Physik **74**, 575 (1932); Ramsauer and Kollath, Ann. der Physik, **17**, 755 (1933).

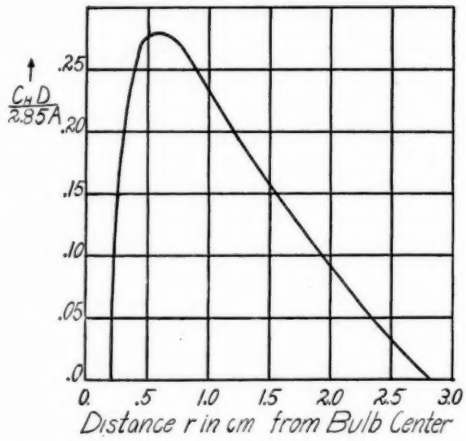

FIG. 2. Concentration of H atoms as a function of the distance from the center of the reaction vessel.

But if the electronic state ψ_ϵ' is the same as that of ψ_ϵ, i.e., there is no electron jump, then

$$\int\overline{\psi_\epsilon'}(r_1^{-3}-r_2^{-3})\psi_\epsilon d\tau_\epsilon=0 \tag{22}$$

since ψ_ϵ is either symmetric or antisymmetric with respect to an interchange of nuclei. There are, therefore, no matrix components connecting ortho to para H_2^+ except with electron jumps, and it follows that there cannot be any spin isomerization except during these electron jumps or during collisions with other molecules. The electron jumps require a considerable amount of activation energy and are, therefore, unimportant.

We next consider the probability of spin isomerization during collisions. Wigner's treatment of paramagnetic gases applies in this case without alteration. The exact position of the electron at the time of the collision is relatively unimportant as long as the electron does not spend a large portion of its time in the neighborhood of the nuclei. From the magnitude of the hyperfine structure separations in atoms, it is found that at the nucleus the magnetic field produced by the spin of an electron in a 1s orbit, corresponds to the electron magnetic moment at a distance of one Bohr radius from the nucleus. We can, therefore, feel confident that the transfer of an electron during collision could not change the order of magnitude of the probability of spin isomerization. Using Wigner's formula, the

probability, W, of spin isomerization taking place during a single collision is

$$W=\frac{a_{H_2}{}^2\mu_\epsilon{}^2\mu_p{}^2}{3(h/2\pi)^2 10^{-48}a_s{}^6v^2}=1.840\cdot 10^{-11}a_s{}^{-6}. \quad (23)$$

Here a_s is the distance of closest approach in A. Since a_s is always greater than unity, it is evident that each H_2^+ would have to have a preposterously long lifetime in order to affect the spin-isomerization. We find, therefore, that H_2^+ can in no way contribute to M/N by direct conversion.

The probability that H_3^+ will convert ortho into para hydrogen is completely negligible. Using the Wigner formula, we find that this conversion probability during a collision would be 10^{-6} that of H_2^+ since we must replace μ_ϵ by μ_p for this case, and of course $\mu_\epsilon/\mu_p\sim 1845$.

The probability that H atoms will convert ortho into para hydrogen without exchange of atoms is, on each collision: $W=1.84\times 10^{-11}a_s{}^{-6}$. The collision diameter of H_2 is 2.3A, and we may therefore take $a_s=2$A. Hence $W=3.0\times 10^{-13}$. We shall show that the mean lifetime of each H atom in the radiochemical experiment is less than one second and during this time it will suffer around 10^{11} collisions. Therefore the probability that a H atom will convert an H_2 molecule magnetically is less than three percent, and the M/N from this source is about one-tenth, i.e., completely negligible in comparison to the total $M/N\sim 1000$.

3. Ortho-para conversion by atomic hydrogen exchange

There remains for consideration only the influence of atomic hydrogen on the conversion process by the exchange reaction, and the data of the two previous sections indicate that this must be of major importance. The atomic hydrogen is produced in the ionization, excitation and neutralization processes already discussed. The net effect of the atomic species must depend on the relative rates of the exchange reaction, $H+H_2(p)=H_2(o)+H$, and the processes which remove atomic hydrogen from the system. Capron's data seemed to indicate that his reproducible results were obtained when the system contained the saturation concentration of mercury vapor. We, therefore, examined, by statistical mechanics, the equilibrium in the system Hg+H=HgH and find that, at the low partial pressure of mercury vapor involved, the equilibrium is predominantly on the free atom side, so that, even though the *velocity* of interaction of Hg and H to form mercury hydride is competitive with the exchange process, no substantial diminution in H atom concentration can thereby be secured, since the molecule immediately dissociates again.

The intensity of alpha radiation falls off with the square of the distance from the source of radiation. To the approximation that the ionization is uniform over the alpha particle range between the source and outer wall, the H atoms formed in unit time per unit volume vary in the same manner. The concentration of atoms is depleted by diffusion of the atoms to the walls and also by three body recombinations with H_2 as the third body. At the stationary state the following equation must be satisfied:

$$\frac{dC_H}{dt}=0=-D\left[\frac{d^2C_H}{dr^2}+\frac{2}{r}\frac{dC_H}{dr}\right]-k_1C_{H_2}C_H{}^2+\frac{aI}{4\pi(R_1-R_2)r^2}. \quad (24)$$

Here, D is the diffusion coefficient of H in H_2 gas. I is the total number of ion pairs produced per second in the reaction system and a is the total number of H atoms from all sources which are associated with the production of each ion pair. R_1 is the radius of the reaction sphere and R_2 that of the radon bulb. The rate constant, k_1, is the well-known constant for the three body recombination of H atoms on an H_2 molecule. Actually, this process is negligible compared to the diffusion process as will presently be demonstrated. Assuming that $k_1C_{H_2}C_H{}^2$ can be neglected, the expression becomes

$$\frac{d^2C_H}{dr^2}+\frac{2}{r}\frac{dC_H}{dr}+\frac{A}{r^2}=0, \quad (25)$$

where $A=aI/4\pi(R_1-R_2)D$. The solution may be written in the form

$$C_H=B-C/R-A\log R, \quad (26)$$

in which the constants B and C are determined in the following way. The concentration at the

wall may be taken as the number of H atoms reaching one square cm of the wall per second, $D(dC_H/dr)$, divided by the average velocity v, or $(D/v)\cdot(dC_H/dr)=\lambda(dC_H/dr)$. Here λ is the mean free path. Introducing this value into (26) for the concentration at the inner and outer wall, we obtain, after omitting negligibly small quantities:

$$C_H=\left[-\frac{R_1R_2}{R_1-R_2}\left(\log\frac{R_1}{R_2}\right)\frac{1}{r}+\log R_1 + \frac{R_2}{R_1-R_2}\log\frac{R_1}{R_2}-\log r\right]A$$

$$=\frac{aI}{4\pi D(R_1-R_2)}\left[-\frac{R_2}{R_1-R_2}\left(\log\frac{R_1}{R_2}\right)\times\left(\frac{R_1}{r}-1\right)+\log\frac{R_1}{r}\right]. \quad (27)$$

From this equation we see that our assumption amounted to taking the concentrations as zero at the two boundaries. A plot of C_H against r is shown in Fig. 2. The factor $D/2.85A$ occurs in the diagram since A varies with the individual experiments and there is some uncertainty as to the best value of D.

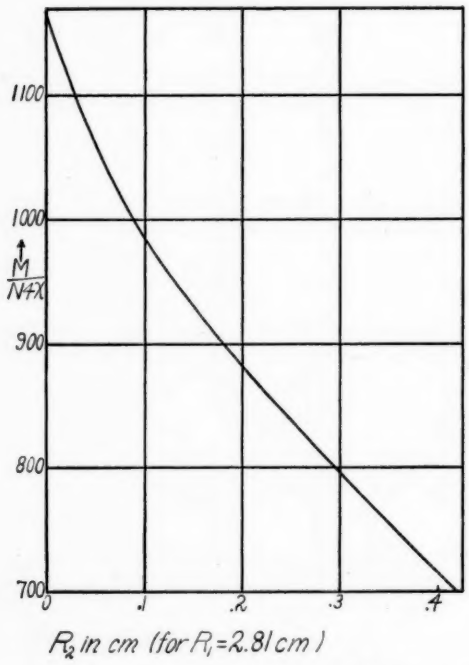

FIG. 3. M/N yield as a function of the radius of the reaction vessel. The ordinate should read M/NaX.

Since the amount of ortho-para conversion per hydrogen atom is directly proportional to its mean life we require this latter quantity. It is evidently the number of hydrogen atoms in the vessel divided by the number formed by the alpha-particles, aI. The total number of hydrogen atoms H_T in the vessel is given by

$$H_T=4\pi\int_{R_2}^{R_1}C_Hr^2dr$$

where C_H is the expression already obtained. Hence

$$H_T=\frac{aI}{D(R_1-R_2)}\left[\frac{1}{9}(R_1^3-R_2^3) - \frac{1}{6}R_1R_2(R_1+R_2)\log\frac{R_1}{R_2}\right] \quad (28)$$

and the mean life

$$\tau=H_T/aI. \quad (29)$$

Now, the rate of reaction $H+H_2(p)=H_2(o)+H$ at room temperature is given by the expression: rate $=(3/4)\times8.5\times10^7(C_H)(C_{H_2})$, or $2.59\times10^3(C_H)$, i.e., each H atom converts 2590 molecules per second with $(C_{H_2})=1$ atm. From the values of τ calculated from the above expression for various values of R_1 and R_2 we have constructed Figs. 3 and 4, in which M/N is set equal to $2590\tau aX$. The value of a, in accord with the conclusions of previous sections, is assigned the value ~6. The quantity X is the fraction of the total hydrogen present in the para form in excess of the equilibrium para concentration. Since Capron studied the conversion of 50 percent ortho: 50 percent para to the equilibrium mixture 75 percent ortho: 25 percent para, the value of X in his work was never in excess of $\frac{1}{4}$. Fig. 3 shows the variation in M/N as a function of the radius of the reaction vessel with the radius of the radon bulb constant at 0.2 cm. Fig. 4 shows M/N as a function of the radius of the radon bulb at a constant radius, R_1, of the quartz reaction vessel which we computed from Capron's reaction volume, 92 cc, to be 2.81 cm. It will be seen that the M/N yield calculated is exactly in the range

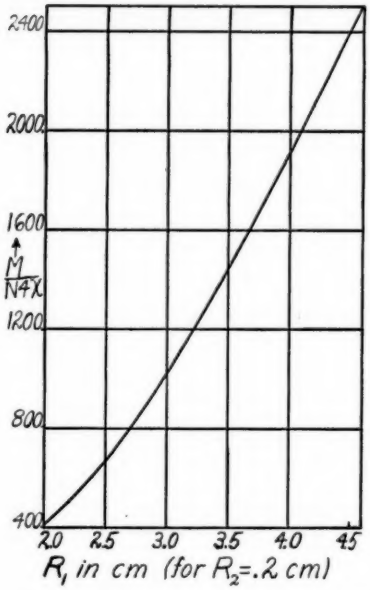

FIG. 4. M/N yield as a function of the radius of the capsule containing the radioactive material. The ordinate should read M/NaX.

of Capron's experimental observations when $a=6$ and the concentration of parahydrogen is $\sim 1/6$. The values calculated depend obviously on the value assigned to D, the diffusion of H atoms in H_2; we have used a value $D=1.94$ cm/sec. which we derive from a value given by Smallwood[24] without reference to source. Alteration of this value will produce proportionate small variations in the value of M/N, as may be seen from equation (27) et seq.

For the homogeneous recombination of atomic hydrogen we use the expression, $k_1 C_H^2 C_{H_2}$, and, for the reaction constant k_1, use the value 10^{16} cm^6 mol^{-2} sec.$^{-1}$.[25] This gives a velocity $v=10^{16}\times(3.74\times10^{-13})^2\times(2.46\times10^4)^{-1}=5.69\times10^{-14}$ moles cc^{-1} sec.$^{-1}$. This represents a fraction

$$v/a(I/\text{volume})=5.69\times10^{-14}/6\times(2.75\times10^{-13})=0.034$$

of the atomic hydrogen which is produced, a negligible fraction as already assumed. In the preceding expression we have used six times the experimentally observed number of ion pairs as the total number of H atoms produced or disappearing per unit time. This alteration in the relative importance of wall and three body removal in the gas phase is caused by the low concentration of atomic hydrogen ($\sim 10^{-13}$ mole cc^{-1}). In the case investigated by Farkas and Sachsse[26] using excited mercury as the source of atomic hydrogen the gas phase reaction was alone important at pressures above 200 mm since the H atom concentration in their studies was $\sim 10^{-10}$ mole cc^{-1}.

The fact that the major removal of atomic hydrogen is at the vessel walls accounts for the observation of Capron that the M/N yield was dependent on the radon intensity and not on the square root of the intensity as would be required by the homogeneous recombination of atoms. The calculations of this section serve to show that the actual para hydrogen conversion is mainly governed by the dimensions of the radon bulb and the reaction vessel and the total pressure. Increase in the radon bulb size would increase the M/N yield. The calculations have been based on the assumption that the walls have a 100 percent efficiency of recombination. The observations of Capron would indicate that this is true when mercury is present but that in the absence of mercury, some reflection from the wall surface occurs with increased, though erratic, conversion.

We wish to express our appreciation for a grant-in-aid from the Penrose Fund of the American Philosophical Society and for facilities granted to one of us (J. O. H.) by the Institute for Advanced Study, Princeton, N. J.

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The Electron Affinity of Bromine Atoms from Space-Charge Effects

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The electron affinity of bromine atoms has been determined from the space-charge effects of a hot tungsten filament in bromine vapor and is found to be 88±3.4 kilocalories.

INTRODUCTION

THE electron affinity of bromine atoms has been determined by the method previously used with iodine.[1] The experimental set-up and methods of procedure were the same as those described. If it is assumed that equilibrium is attained between bromine atoms, electrons and bromine ions on the surface of the filament then the electron affinity $(-\Delta E_0)$ of bromine is given by the expression

$$-\Delta E_0 = 4.575 T_s(\log F - \log P\ (Br_2, \text{mm}) + 2 \log T_s + 0.972),$$

where T_s = temperature of the filament, F = ratio of currents carried by bromide ions and electrons and $P\ (Br_2, \text{mm})$ = the pressure of bromine molecules in the reaction tube in mm Hg.

RECENT DETERMINATIONS

The electron affinity of bromine atoms is given by Mayer and Helmholz[2] as 81.5 kilocalories or 3.55 electron volts on the basis of thermochemical calculations involving the lattice energies of several alkali bromides. Piccardi[3] determined the conductivity of a flame fed with ethyl bromide and he reports 86.7 kilocalories or 3.76 electron volts for the electron affinity of bromine atoms.

EXPERIMENTAL RESULTS

The first determinations were carried out with bromine purified by shaking with several portions of normal potassium hydroxide solution and drying by distilling twice through phosphorus pentoxide. The last fractions of bromine were kept in the hope that the more volatile chlorine would be removed by this treatment. The bromine was distilled into small tubes carrying a breaking device through which they could be attached to the diode.[1] On breaking the shut-off, with liquid air on the bromine, a pressure developed in the experimental tube. The plate current was high and unsteady. The current-potential curves ($\log i - \log V$) showed a discontinuity at about 18 ev because of ionization of gas in the tube. This jump was far too great to correspond to the bromine pressure, judging from the experiments on iodine. Finally the conclusion was reached that the method of purification employed was insufficient to remove all the chlorine present as an impurity. The scheme adopted for the complete separation of the chlorine was to pump off all residual gases from the bromine supply at →100°C where the chlorine pressure is still about 4 mm Hg. The experiments reported in Table I were carried out on bromine purified in this manner.

A sample run is shown in Fig. 1 where the logarithm of the current in milliamperes is plotted as a function of the logarithm of the plate voltage. The three-half-power law is not obeyed but the relations between the currents in vacuum and with bromine in the tube and the

TABLE I.

Bromine °C	Bromine $P(\text{mm})\times10^5$	Filament Temperature T_s	Current Ratio $F\times10^5$	Electron Affinity $-\Delta E_0$
−99.5	94	2310	1164	92.5
"	94	2410	276	90.5
−94.5	242	2419	190	84.6
"	242	2293	303	82.0
−99.5	94	2308	362	86.0
"	94	2432	370	92.0
−94.5	242	2432	748	91.5
"	242	2324	1288	89.5
−78.0	3350	2324	3550	82.0
−77.5	3610	2463	6270	89.6
				88.0±3.4 kilocalories

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plate voltage are sufficiently linear to permit extrapolation and determination of the constants of the diode.

Discussion of Results

It is seen that the value found for the electron affinity of bromine atoms in the present experiments agrees with the only other *direct* experimental determination of Piccardi.[3] However it was hoped that the indirectly found value of Mayer and Helmholz[2] could be checked, because they obtained their result from several bromides. It is conceivable that the bromine used by us was not of sufficient purity. The experiments reported here will be repeated at some future time and it is hoped that by using further extraordinary precautions it will be possible to give a definite answer. Since it is impossible to tell at the moment when this research can be continued, it was thought proper to report the present findings.

We are indebted to the research grant committee of the Graduate School of the University of Minnesota for financial assistance which enabled us to carry out this investigation.

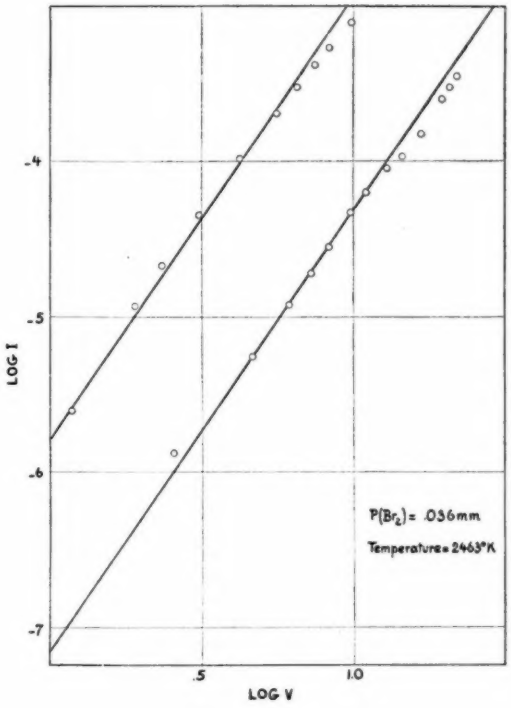

Fig. 1. Current-potential curve in vacuum and in bromine gas.

AUGUST, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

VI. The Methanol Equilibrium[1]

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(Received May 23, 1936)

The entropy of methanol and the equilibrium constant for methanol synthesis are calculated for two molecular models, one of which rotates freely about the CO bond, while the other possesses a torsional oscillation of frequency 700 cm^{-1} about that bond. The latter model is indicated by spectroscopic evidence and gives an entropy in close agreement with the third law value and an equilibrium constant close to the mean of the widely scattered experimental results. The former model is supported strongly by valence theory; it can be made to agree with the third law entropy by assuming a zero-point entropy of $R \log 3$, and its rather poor agreement with experimental equilibrium data is not conclusive evidence against it. The true equilibrium constant probably lies between these two calculated values, or at worst slightly beyond one of them.

THE equilibrium constant for the reaction

$$2H_2+CO=CH_3OH$$

has been determined many times. The extreme values at a single temperature are in some cases in the ratio of eight to one, and there is little reason to have confidence in the average values. This is particularly so because of the occurrence of undesired side reactions. It is

[1] Contribution from the Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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therefore of considerable interest to determine whether a more accurate value can be calculated from spectroscopic data.

Unfortunately neither the configuration nor the vibration frequencies of methanol are completely known. Pauling and Brockway[3] found from electron-diffraction measurements with methyl ether a CO distance of 1.42×10^{-8} cm and a COC angle of 111°. Reasonable values for the water molecule, based on spectroscopic data, are 0.95×10^{-8} cm for the OH distance and 105° for the HOH angle. The value of 110° for the COH angle is used in the following calculations, together with distances $d_{CO}=1.42\times10^{-8}$ cm, $d_{OH}=0.95\times10^{-8}$ cm, $d_{CH}=1.11\times10^{-8}$ cm. The carbon valences are assumed to be at exact tetrahedral angles. It is then easy to calculate, using methods which have previously been developed,[4] that if there is free rotation about the CO bond the translation-rotation entropy is

$$S_{t+r}=6.375+(9/2)R\log T,$$
$$S_{t+r,\ 298}=57.316,$$

while if this rotation is completely inhibited, the entropy is

$$S_{t+r}=10.089+4R\log T,$$
$$S_{t+r,\ 298}=55.370.$$

The most complete analysis of the vibration spectrum is that of Bartholomé and Sachsse,[5] who give

$\nu(\pi)_{CH}$	2943–2835 cm^{-1}	(resonance with $2^2\delta(\sigma)_{CH}$)
$^2\nu(\sigma)_{CH}$	3000	
$\delta(\pi)_{CH}$	1360	
$^2\delta(\sigma)_{CH}$	1470	
ν_{OH}	3400	
ν_{CH_3-OH}	1025	
^{3} or $^4\delta_{CH_3-OH}$	690, 725, —, —.	

The δ_{CH_3-OH} vibration will be triple if there is free rotation, quadruple if the rotation is frozen. Bartholomé and Sachsse consider that the appearance of the spectrum favors the latter alternative. They propose 700 cm^{-1} as a probable value for both unobserved δ_{CH_3-OH} frequencies. One of these frequencies corresponds to torsion about the CO bond, however, and in order to have a torsion frequency of this magnitude, it is necessary for the potential energy barrier opposing free rotation to be at least 3000 cal. For the somewhat similar case of ethane, Eucken and Weigert[6] calculated from low-temperature specific-heat measurements a potential barrier of 315 cal., and Eyring[7] estimated 350 cal. from valence theory. A calculation similar to Eyring's gave 300 cal. for the potential barrier in methanol. This value might be somewhat increased by the effect of the OH dipole moment, but it scarcely seems possible to account for a value of 3000 cal. in that way. In view of this difficulty in understanding such a high torsion frequency, calculations will be made for two cases: (a) free rotation and three δ_{CH_3-OH} frequencies at 700 cm^{-1}; (b) inhibited rotation and four δ_{CH_3-OH} frequencies at 700 cm^{-1}.

For the hypothetical perfect gas at atmospheric pressure, with free rotation $S_{298}=58.38$ and without free rotation $S_{298}=56.74$. The third-law value found by Kelley[8] for the liquid is $S_{298}=30.26\pm0.2$. From this value, the vapor pressure,[9] and the very accurate heat of vaporization determined by Fiock, Ginnings and Holton,[10] the value for the gas is $S_{298}=56.63$. The third-law entropy is based on specific-heat measurements down to 16.5°K, and Kelley's estimate of error for it seems reliable. The calculation of ΔS_{vap} should be correct to within 0.05 e.u. If the COH angle were 115° instead of 110°, the entropy of the freely rotating molecule would be reduced by 0.07 e.u. A uniform decrease of all bond distances by five percent would reduce the entropy by 0.39 e.u. The total vibrational contribution of 1.06 e.u. depends to the extent of 0.75 e.u. on directly observed frequencies, hence is certainly not more than 0.31 e.u. too high. The cumulative effect of all these very liberal estimates reduces the disagreement between the third-law result and the calculated value for free rotation from 1.75 e.u. to 0.73 e.u. This is still markedly unsatisfactory. The third-law result,

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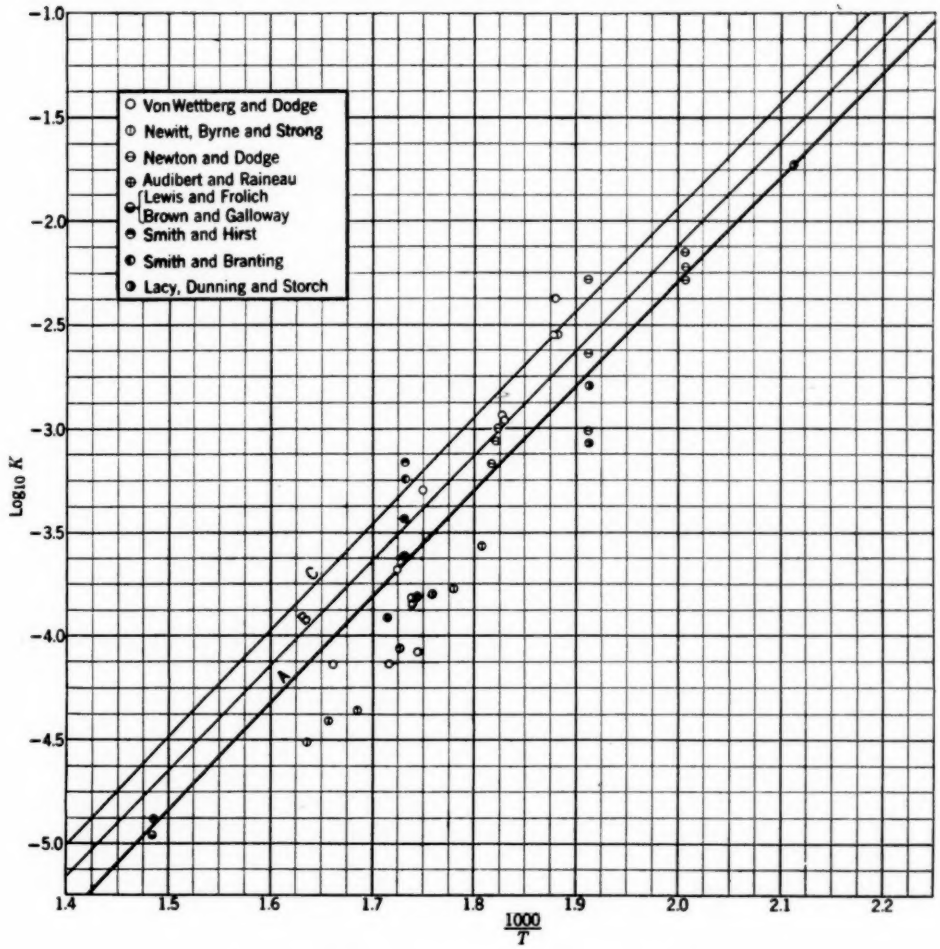

FIG. 1. Equilibrium constants for methanol synthesis.

however, can be reconciled with free rotation about the CO bond by assuming that because of lack of order in the actual crystal there is an unmeasured entropy of R log 3 or slightly less. The corrected third-law value is then 58.81 e.u., or somewhat less than this value if there is partial ordering; the agreement with the theoretical value of 58.38 e.u. is sufficiently good. The very good direct agreement of the third-law value with the calculation based on lack of free rotation is to some extent fortuitous, since the estimate of 700 cm^{-1} for the two unobserved frequencies may well have introduced an error of several tenths of an entropy unit. This agreement, nevertheless, certainly provides evidence in favor of torsion rather than free rotation about the CO bond.

Since it is hard to understand the existence of a potential barrier high enough to permit even one excited state of CO torsion, it is probable that higher states will be rotational. Lack of knowledge as to these higher states limits the temperature range within which reasonably accurate calculations for the torsion model can be made. At 750°K, however, where $-F/T$ for a harmonic oscillator with frequency 700 cm^{-1} is 0.606, $-F/T$ for a system with only one excited level 700 cm^{-1} above the normal is 0.464. The position and character of the higher levels thus cannot make any great difference up to this temperature.

Table I gives $-(F^\circ - E_0^\circ)/T$ for methanol and $\log_{10} K$ for $2H_2+CO=CH_3OH$ up to 750°K for both torsion and free rotation models. In making

TABLE I. *"Free energy" and equilibrium constant for methanol.*

T, °K	Torsion $-(F°-E_0°)/T$	Torsion $\log_{10} K$	Free Rotation $-(F°-E_0°)/T$	Free Rotation $\log_{10} K$
298.1	47.716	4.322	48.602	4.680
300	47.774	4.221	48.663	4.578
350	49.208	1.939	50.205	2.297
400	50.518	.199	51.594	.557
450	51.738	−1.175	52.874	− .818
500	52.884	−2.288	54.064	−1.932
550	53.975	−3.207	55.186	−2.853
600	55.012	−3.980	56.246	−3.629
650	56.009	−4.638	57.258	−4.290
700	56.962	−5.207	58.220	−4.862
750	57.875	−5.703	59.139	−5.361

these calculations, $-F/T$ for hydrogen has been taken from the tabulation of Giauque,[11] and H from that of Davis and Johnston.[12] For carbon monoxide the revised $-F/T$ values of Clayton and Giauque[13] are used, and H is taken from the work of Johnston and Davis.[14] Rossini's accurate values are used for the heats of combustion of hydrogen,[15] carbon monoxide,[16] and gaseous methyl alcohol.[17] Curve A in Fig. 1 reproduces the equilibrium constants calculated for the torsion model, and curve C those for free rotation. The points represent experimental results of Lewis and Frolich,[18] Brown and Galloway,[19] Audibert and Raineau,[20] Smith and Branting,[21] Newitt, Byrne and Strong,[22] Lacy, Dunning and Storch,[23] Smith and Hirst,[24] von Wettberg and Dodge[25] and Newton and Dodge,[26] all corrected to zero pressure by Newton and Dodge.

The agreement of curve C with the experimental results can scarcely be considered good, but it would require considerable courage to reject the assumption of free rotation on that basis alone.

Curve B is included to show the effect of shifting the two unobserved frequencies for the torsion model from 700 cm^{-1} to 500 cm^{-1}. The displacement of the equilibrium constant is relatively unimportant, but the calculated entropy becomes $S_{298}=57.45$, in rather definite disagreement with experiment.

It does not appear possible at present to reach any final decision with regard to rotation about the CO bond. Evidence in favor of a torsional oscillation about this bond is provided by the absorption spectrum, the entropy, and rather feebly by the equilibrium constant. Valence theory, however, seems to demand free, or very nearly free, rotation about this bond; this model can be harmonized with third-law results by assuming a zero-point entropy of $R \log 3$, and is not entirely incompatible with equilibrium data. Aside from the uncertainty about this one point, there does not seem to be much possibility of any considerable error in the calculations. The true equilibrium constant, therefore, should lie between curves A and C, or at worst slightly outside those limits.

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Kinetics of Recombination of Iodine Atoms

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(1) The equilibrium $I_2+h\nu \rightarrow I+I$; $I+I \rightarrow I_2$ was studied in presence of different foreign gases by means of a sensitive optical arrangement. (2) The equilibrium is a "heterogeneous" one at low pressure, the atoms recombining mainly by diffusing to the walls. In this region, the dissociation increases with rising pressure. (3) At higher pressure (about 250 mm in He, 40 mm in CO_2, etc.), the recombination becomes homogeneous. The transition is a sharp one, and practically no influence of the walls is observed at pressures above the transition point. (4) In the region of homogeneous recombination, the dissociation is exactly proportional to the square root of light intensity and to the inverse square root of pressure, in accordance with the theoretical formulae for the "recombination by three-body collisions," $I+I+X \rightarrow I_2+X$. (5) The velocity constants of these reactions are calculated for different gases X. The values are given in Table IV. The order of increasing efficiency in promoting recombination is He, A, H_2, N_2, O_2, CH_4, CO_2, C_6H_6. One double collision I+I in 530 is a recombining one in helium, and one in 50 in carbon dioxide at atmospheric pressure. (6) The efficiency as third body is higher for the di- and polyatomic molecules than for the monoatomic ones, and increases with growing molecular size and the intensity of the molecular fields of the colliding particles.

I. INTRODUCTION

WHEN a closed vessel containing iodine vapor (pure or mixed with some "neutral" foreign gas) is uniformly illuminated, three processes take place simultaneously:

(a) Light is absorbed and converted into heat. A temperature gradient is established between the center of the vessel and the walls. The concentration of the I_2 molecules is lowered near the center and raised near the walls. We call these phenomena briefly "the thermal effect."[1]

(b) Iodine molecules are dissociated into atoms: "dissociation effect." At low concentrations, the atoms migrate to the walls, recombine there and return as molecules into the gas. As a result, the stationary concentration of iodine molecules is lowered everywhere in the vessel, but especially near its center: "heterogeneous dissociation equilibrium."

(c) At higher pressures, the atoms recombine in the gas phase itself. As a consequence, the stationary concentration of the iodine molecules is lowered uniformly throughout the vessel: "homogeneous dissociation equilibrium."

We are, above all, interested in the last effect, because it permits the determination of the velocity of recombination of free atoms in the gas phase—an elementary process playing an important role in a great number of chemical reactions.

II. EXPERIMENTAL

In a previous paper[2] we described a sensitive optical arrangement which permits the measurement of the stationary change in concentration of halogen molecules in an illuminated vapor. Fig. 1 will recall the principle of the method; details of the optical and electrical arrangements can be found in the above-mentioned paper.

The experiments consist in measuring the change ΔI in the intensity of the light beam I from the lamp (7) which occurs when shutter (2) is opened and iodine vapor in the rectangular cell (6) is uniformly illuminated by the light L from a 1500-watt automatic carbon arc (1); and the reverse change which follows the closing of the shutter. The method, first[2] used for experiments with bromine vapor, was later[3] improved in experiments with iodine *solutions*. In applying it to iodine *vapor*, we found that we were now able to detect optical effects of the order of $\Delta I/I=2\times10^{-5}$. The error in measuring effects of the order of $\Delta I/I=0.001$ now does not exceed 1 percent.

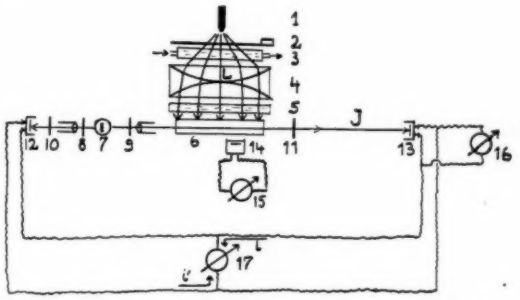

FIG. 1. Scheme of the apparatus: 1. Arc, 2. shutter, 3. running water, 4. condenser, 5. $CuSO_4$-solution, 6. reaction-vessel, 7. 6v-lamp, 8, 9, 10, 11. glass-filters, 12, 13. photo-cells ("electro-cell"), 14. thermopile, 15. galvanometer, 16. microammeter, 17. Zernicke-galvanometer.

[1] The pressure in the vessel is also increased. This side of the phenomenon is known as "Budde effect."

[2] E. Rabinowitch and H. L. Lehmann, Trans. Faraday Soc. **37**, 689 (1935).

[3] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 547 (1936).

A. Measurement of the Effect

The total light intensity I transmitted through the cell (6) is measured by means of the photo-cell (13) with the microammeter (16); the intensity change ΔI by means of the same photo-cell with the galvanometer (17) (Zernicke Zc, sensitivity 1.25×10^{-10} amp. per mm). For measuring ΔI, the photo-current i is compensated by the current i' from a second photo-cell (12) illuminated by the same source. To eliminate the irregular fluctuations of the galvanometer which are observed after the compensation of the currents i and i', a set of measurements of ΔI was made, usually consisting of ten "openings" and ten "closings" of the shutter. Fig. 2, shows a typical result; the ordinates are the successive readings of the galvanometer, circles corresponding to the shutter being open, points to it being closed. The effect is, in this particular example, $\Delta\bar{I}=39.5$ mm and the fluctuations are of the order of 2 mm only.

From the relative change in transmission $\Delta I/I$ the relative change in concentration, $\Delta\equiv\Delta[I_2]/[I_2]$, is calculated by means of the following equation:

$$\Delta I/I=\Delta\bar{\alpha}_I p_{\text{atmos}}\, d \ln 10. \qquad (1)$$

$\bar{\alpha}_I$ is the mean extinction coefficient of iodine for the light $I(I=I_0 10^{-\alpha p_{\text{atmos}} d})$, p_{atmos} the iodine pressure in atmospheres and d the length of the cell. Eq. (1) is exact for monochromatic light only. It can be used, with a mean extinction coefficient $\bar{\alpha}$, for nonmonochromatic light, as long as the absorption remains small throughout the spectral region concerned. In our experiments, the absorption was 10 percent on the average and not over 15 percent in the part of the spectrum corresponding to the maximum of the extinction curve of iodine (5200A).

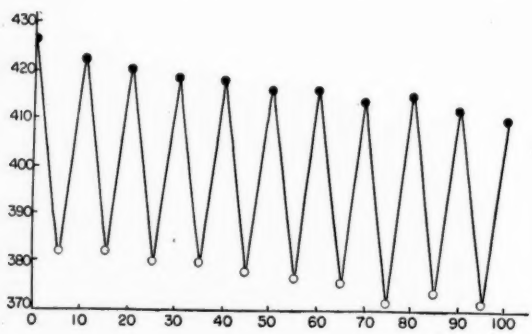

FIG. 2. Results of a single run.

To obtain the highest values of ΔI, it is necessary to use light with the highest $\bar{\alpha}$ value compatible with a sufficiently high intensity I. We used light from a 6-v filament lamp filtered through Jena infrared absorbing glass—(8) and (9) in Fig. 1—and Wratten color filter No. 45—(10) and (11)—(transmitting wave-lengths 4400–5200A).

The mean extinction coefficient of iodine for this light is $\bar{\alpha}_I=19.7$ in vacuum, or $\bar{\alpha}_I=22.0$ in presence of foreign gases. The difference is due—as discussed in another paper[4]—to the fact that part of the light transmitted by filter No. 45 belongs to the band region ($\lambda>4990$A).

B. Determination of the Number of Quanta

The number of quanta absorbed per second in 1 cc of the gas, $N_{h\nu}$, is computed by measuring the intensity of the light L behind the vessel (6), by means of the thermopile (14) connected with the galvanometer (15). Great care was taken to calculate $N_{h\nu}$ as exactly as possible. The concentration of iodine, $p(\mathrm{I_2})$, the mean extinction coefficient of iodine for the light L, $\bar{\alpha}_L$, and the mean wave-length of the light absorbed, $\bar{\lambda}_L$, are the three quantities required for the calculation.

(a) The *iodine concentration* was computed from the vapor pressure curve of solid iodine given by Baxter, Hickey and Holmes.[5] The iodine vapor was introduced from a slightly cooled container ($t=15-16$°C) into the highly evacuated vessel (6). Measurement of the absorption of the light I gave an independent control of the quantity of I_2 in the vessel. During the experiment the reaction vessel was closed by a stopcock lubricated with colloidal graphite and phosphoric acid.

(b) The mean extinction coefficient $\bar{\alpha}_L$ was calculated from the spectral distribution curve of the light L, determined by means of a Hilger quartz double monochromator and a thermopile. The mean extinction coefficient was computed by graphical integration, according to the equation:

$$\bar{\alpha}_L=\int_0^\infty I_\lambda\alpha_\lambda d\lambda/\int_0^\infty I_\lambda d\lambda. \qquad (2)$$

The values of α_λ were determined and published by us elsewhere.[4] It was shown previously,[6] that the quantum yield of dissociation of I_2 is equal to 1, not only in the continuous

[4] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 540 (1936).
[5] Baxter, Hickey and Holmes, J. Am. Chem. Soc. **29**, 127 (1907).
[6] E. Rabinowitch and W. C. Wood, Chem. Phys. **4**, 358 (1936).

region of the spectrum, but also in the band region (provided the pressure is high enough to suppress fluorescence). We used therefore in the following experiments continuum and band region together, in order to obtain the highest effects possible. The light L was filtered only through 10 mm of a saturated $CuSO_4$ solution (5). The energy distribution of this light is shown in Fig. 3. (The maxima are due to CN-bands.) The lower curve shows the spectral distribution of the light absorbed by iodine. The mean extinction coefficient $\bar{\alpha}_L$ is calculated as a quotient of the areas under both curves:

$$\bar{\alpha}_L = 18.0.$$

The use of a mean coefficient is quite safe in this case, because the total absorption across the cell ($d = 2$ cm) is of the order of two percent only. The values of α_λ used in (2) for the band region are the ones corresponding to the "limiting" extinction curve (as defined in reference 4). The absorption is so small that even in absence of foreign gases no sensible deviations from this curve can be expected.

(c) The mean wave-length of the light absorbed, $\bar{\lambda}_L$, was determined in an analogous way, by graphical integration:

$$\bar{\lambda}_L = \int_0^\infty I_\lambda \alpha_\lambda \lambda d\lambda / \int_0^\infty I_\lambda \alpha_\lambda d\lambda. \quad (3)$$

The value $\bar{\lambda}_L = 5180$A was found in this way. The thermopile (14) was calibrated with the galvanometer (15) by means of a tungsten filament standard lamp of the National Physical Laboratories and a carbon filament standard lamp of the U. S. Bureau of Standards. Both calibrations gave identical values.

As a result of these measurements, the formula:

$$N_{h\nu} = 11.2 \times 10^{13} p_{\mathrm{mm}}(\mathrm{I_2}) L \text{ cm (quanta/sec. cc)} \quad (4)$$

was obtained, the numerical coefficient incorporating the calibration factor, the reflection corrections and the above determined values of $\bar{\alpha}_L$ and $\bar{\lambda}_L$. L is the deflection of the galvanometer (15) in cm, $p_{\mathrm{mm}}(\mathrm{I_2})$ the iodine pressure in mm. For the low absorptions used, $N_{h\nu}$ is practically proportional to $p(\mathrm{I_2})$.

The *energy* absorbed per second in 1 cc of the gas is:

$$Q = 1.02 \times 10^{-5} \times p_{\mathrm{mm}}(\mathrm{I_2}) L (\text{cal./sec. cc}). \quad (5)$$

In order to obtain a *constant* illumination, the arc was arranged to burn as steadily as possible. With good carbons, a constancy of two percent was obtained. In order to make the illumination uniform all over the surface of the cell (6) (24 cm^2) the latter was placed as close to the condenser lens (4) ($f = 7$ cm, diameter 14 cm) as possible.

A cell with running water (3) and a shutter (2) were placed between the arc and the condenser, glass filters and a cell with $CuSO_4$ solution (5) between the condenser and the reaction vessel (Fig. 1). The total distance between the positive crater and the reaction vessel was not more than 16 cm; nevertheless, two maxima of the light intensity (due to spherical aberration of the lens) were observed at the ends of the vessel and a minimum in the middle. The variations were, however, of the order of ten percent only, and a mean value of L was obtained by placing the thermopile in the position shown in Fig. 1.

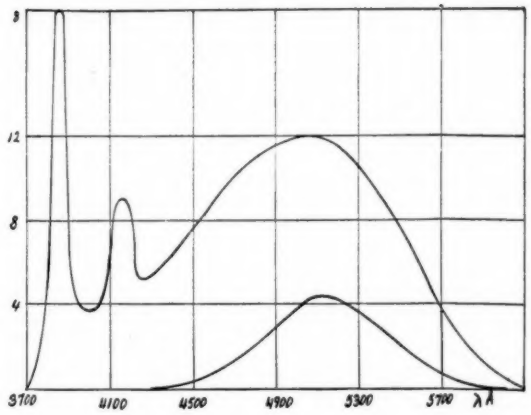

FIG. 3. Intensity-distribution. Upper curve: arc-light filtered through $CuSO_4$. Lower curve: light absorbed by iodine.

To prevent *heating* of (4), (5) and (6) by the arc, shutter (2) was only opened for 10 seconds for each measurement and cooled by a stream of air.

Scattered light from the arc (1), reaching the photo-cell (13) was reduced by screens, by the filter (11) and especially by a long distance (30 cm) between (11) and (13). It caused only a small correction (about 1–3 mm) to be applied to ΔI.

III. FORMULAE; SUPPRESSION OF THE THERMAL EFFECT

The following formulae were derived in reference 2 for the three effects mentioned in the introduction:

(a) Thermal effect

$$\Delta_{\mathrm{therm}} = (3/32)(Q/\kappa T_0). \quad (6)$$

Q is the energy in cal. absorbed in 1 cc of the

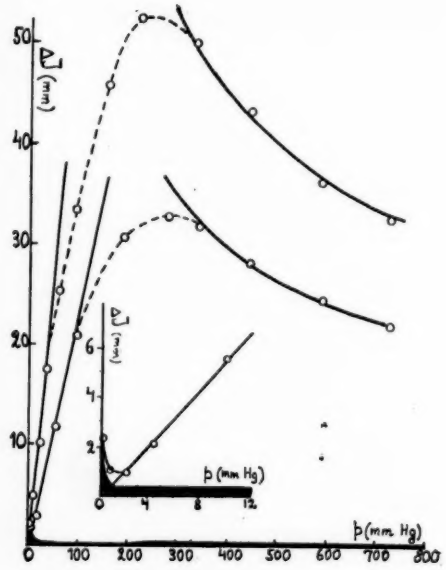

FIG. 4. He and I_2.

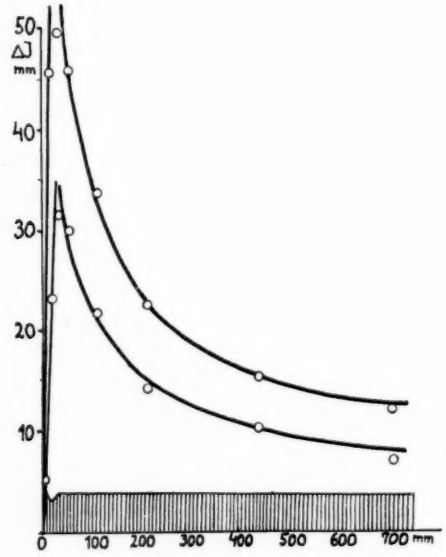

FIG. 5. CO_2 and I_2.

gas per second,—see Eq. (5)—κ the thermal conductivity of the gas, T_0 the temperature of the cell. This formula is derived under two simplifying conditions: (a) an endless cylindrical vessel ($r=1$ cm) is considered instead of actually employed rectangular cell $2\times2\times12$ cm. (b) convection is disregarded altogether. The stationary rise of temperature in the center of the cell, calculated by considering the thermal conductivity alone, was in the following experiments not over 0.05° in hydrogen and helium, and 0.5° in nitrogen and other gases used. The neglecting of convection appears therefore to be reasonable enough. This point has been discussed in more detail elsewhere.[7]

(b) Heterogeneous dissociation equilibrium

The following formula is based on the same simplifications as those underlying formula (6):

$$\Delta_{\text{hetero}}=(5/16)N_{h\nu}p_{\text{atmos}}(\text{X})/D_0[\text{I}_2]. \qquad (7)$$

$p_{\text{atmos}}(\text{X})$ is the pressure of the foreign gas in atmos, and D_0 the diffusion coefficient of iodine atoms into this gas at atmospheric pressure.

(c) Homogeneous dissociation equilibrium

Assuming that the homogeneous recombination occurs by triple collisions only, according to the formulae:

$$\text{I}+\text{I}+\text{X}\rightarrow\text{I}_2+\text{X} \qquad (8)$$

$$-d[\text{I}]/dt=C_1[\text{I}]^2[\text{X}] \qquad (9)$$

the following formula is obtained for the dissociation equilibrium:

$$\Delta_{\text{homo}}=(1/[\text{I}_2])(N_{h\nu}/2C_1[\text{X}])^{\frac{1}{2}} \qquad (10)$$

[X] is the concentration of the gas of which the molecules act as "third bodies."

Under the conditions of our previous work with bromine,[2] the thermal effect dominated the dissociation effect in all gases except helium. In order to be able to calculate C_1 values for all gases, the most important step was to reduce the thermal effect. According to the formulae (6), (7) and (10), this is achieved by *reducing the concentration of the halogen.* Δ (therm) is proportional to $[\text{I}_2]$, whereas Δ (hetero) is independent of $[\text{I}_2]$, and Δ (homo) proportional to $1/([\text{I}_2])^{\frac{1}{2}}$. By using 0.14 mm of iodine instead of 5 mm of bromine (which were used in our previous work) we reduced the thermal effect to about one percent of its former value. In the following experiments, Δ(therm) was only a small correction, which could be calculated according to the approximate formula (6). Its magnitude is shown by the darkened area in Figs. 4 and 5. The small

[7] E. Rabinowitch, Zeits. f. physik. Chemie **B**, to appear shortly.

figure, inset in Fig. 4, represents the beginning of the upper curve on a larger scale. It shows the small increase in ΔI observed at the lowest pressures to be due to an increase in the thermal effect, caused by the low heat conductivity of iodine vapor. Calculations show that thermal effect accounts for the whole of ΔI observed in pure iodine vapor. This and other observations confirm that the estimation of the thermal effect according to (6) is a fairly accurate one—at least at sufficiently low pressures. There are, however, indications that convection currents actually occur at higher pressures, destroying the thermal effect altogether and making the thermal correction unnecessary (see further below).

IV. General Results

Experiments were made with He, A, N_2, O_2, CH_4, CO_2 and C_6H_6. All the laws deduced from the theoretical formula (10) were exactly confirmed.

(a) Dependence of the effect on pressure

Figs. 4, 5 and 6, show typical curves obtained by measuring the optical effect with increasing pressure of a foreign gas, $p(I_2)$, L and I being kept constant. The figures clearly show the existence of two regions. In the *low pressure region* the recombination is a heterogeneous one, and the effect *increases* with pressure (because of the slower diffusion), in accordance with formula (7). In the *high pressure region*, the effect *decreases* with pressure, because of the increasing probability of triple collisions. According to (7), the increase in the heterogeneous region must be a linear one; according to (10) the decrease in the homogeneous region must follow the inverse square root law. These two "theoretical" curves are shown by thick lines in Figs. 4, 5 and 6. One sees that the influence of the homogeneous recombination is more strongly felt in the heterogeneous region (especially in helium) than the influence of the walls in the homogeneous one. The explanation of this difference is given elsewhere.[7]

The position of the maximum depends not only on the nature of the gas, but also on light intensity. The abscissae of the intersection of the two theoretical curves are inversely proportional to L^4; the abscissae of the maximum must change in about the same way.[8] The two curves referring to two different light intensities in Figs. 4 and 5, and also the results obtained with other gases are in accordance with this prediction.

(b) Dependence on light intensity

Two sets of measurements were made with each gas (as shown by Figs. 4 and 5) with light intensities roughly in the relation 2 : 1. In addition, several sets of measurements were made, at constant pressure, with 3 or 4 different light intensities. Figs. 7 and 8 are characteristic

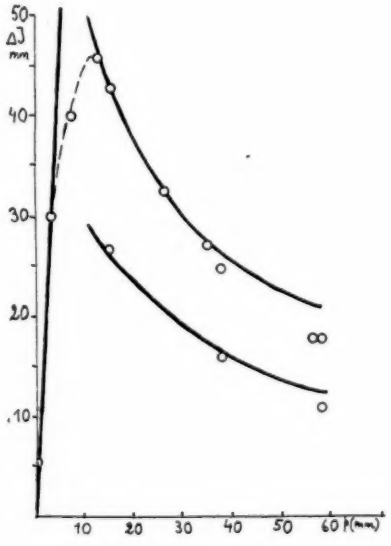

Fig. 6. C_6H_6 and I_2.

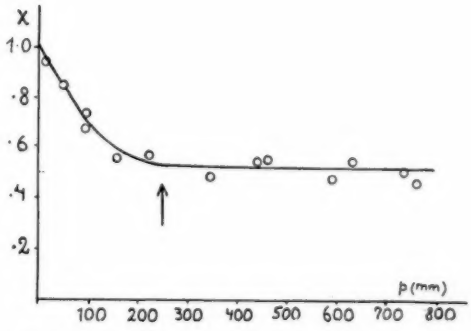

Fig. 7. $He+I_2$. Dependence on light-intensity.

[8] The conclusion that purely homogeneous recombination is more easily obtained at higher light intensities was already drawn by W. Yost, Zeits. f. physik. Chemie **B3**, 95 (1933).

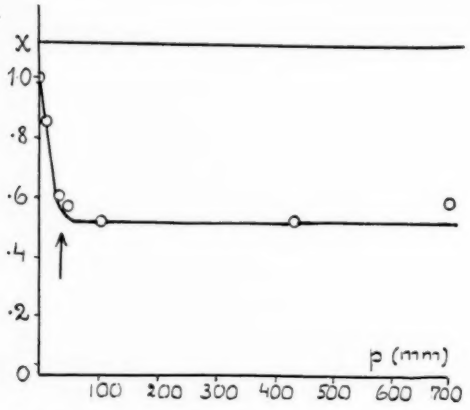

FIG. 8. $He+CO_2$. Dependence on light-intensity.

of the results obtained. They show the exponent x of the equation

$$\Delta I = \text{const} \times L^x \qquad (11)$$

as a function of pressure, for the cases of helium and carbon dioxide which were already used in Figs. 4 and 5. In agreement with (6), (7) and (10), the exponent x drops from the value $x=1$ (which is the theoretical value both for the thermal and for the heterogeneous effect) down to $x=0.5$—which is the theoretical value corresponding to heterogeneous recombination—and then remains constant. The transition occurs at the same pressure as that corresponding to the maxima in Figs. 4 and 5 (indicated by the arrows). These curves show especially clearly that the deviations from the theoretical value are much larger in the low pressure region ($x_{\text{theor.}}=1$) than in the region above the maximum ($x_{\text{theor.}}=0.5$).

(c) Dependence on the nature of the gas

Helium offers the least resistance to diffusion and has the lowest recombining efficiency. The helium curve (Fig. 4), is therefore the one with the flattest maximum, situated at the highest pressures (about 250 mm). *Carbon dioxide* (Fig. 5) shows the opposite extreme-slow diffusion, strong recombination—giving rise to an early maximum (at 40 mm). *Benzene* vapor (Fig. 6) shows a maximum already at 12 mm; but in this case, the inverse square-root law is not so strictly obeyed in the homogeneous region. The properties of the other gases investigated

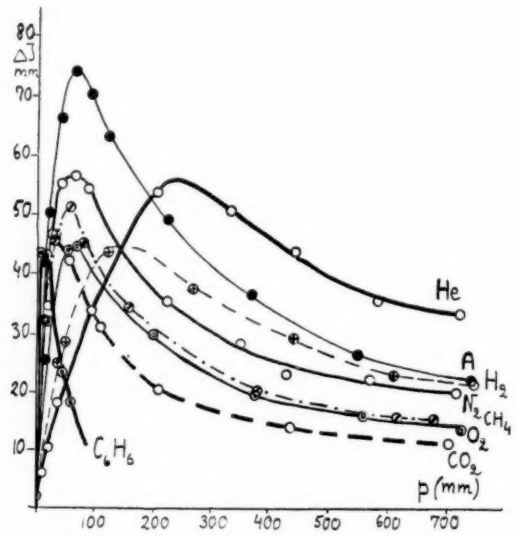

FIG. 9. Summary of the results with different gases.

lie between those of helium and of carbon dioxide. The results are shown (on a smaller scale, and for one light intensity only) in Fig. 9. *Hydrogen* is the nearest to helium. *Argon* combines relatively slow diffusion with relatively slow recombination; the highest dissociation effects can therefore be obtained in this gas. (Not less than 1.6 percent of all iodine molecules are dissociated in the stationary state at $p_A=90$ mm and $N_{h\nu}=1.2\times10^{15}$.)

V. Calculation of the Velocity Constants

Tables I and II contain all data for the calculation of the velocity constants C_1 for the two extreme cases of helium and benzene vapor. Table III gives the summary of the results obtained with all other gases. Only one experiment is used for each gas, although more were made with He, N_2, O_2, CH_4 and CO_2. The mean values obtained in these experiments were always in

TABLE I. *Iodine and helium.* $p(I_2)=0.150$ mm. $I=3.70\times10^4$ mm.

p(He) (mm)	$N_{h\nu}$ $\times10^{-14}$	ΔI (mm)	$\Delta\times10^3$ TOTAL	$\Delta\times10^3$ THERM.	$\Delta\times10^3$ DISS.	C_1 $\times10^{12}$
336	11.6	50.2	11.2	0.10	11.1	1.73
447	11.7	43.6	9.75	0.10	9.65	1.72
	5.54	28.3	6.34	0.05	6.29	1.92
589	11.0	35.1	7.81	0.09	7.72	1.82
	5.36	24.0	5.34	0.04	5.30	1.99
733	11.5	32.8	7.32	0.09	7.23	1.85
	5.60	21.9	4.89	0.04	4.84	2.01
					Mean	1.8 ± 0.1

TABLE II. *Iodine and benzene.* $p(I_2)=0.142$ mm. $I=4.5\times10^4$ mm.

$p(C_6H_6)$ (mm)	$N_{h\nu}$ $\times10^{-14}$	ΔI (mm)	TOTAL	$\Delta\times10^3$ THERM.	DISS.	C_1 $\times10^{32}$
15.1	9.66	42.7	8.08	1.16	6.32	92
	4.56	27.1	5.12	0.55	4.57	99
25.6	9.96	32.5	6.15	1.20	4.95	(109) 71
	4.56	18.4	3.48	0.55	2.93	(142) 101
37.5	9.42	24.7	4.67	1.13	3.54	(137) 78
	4.34	16.0	3.03	0.52	2.51	(125) 86
58.3	9.18	17.8	3.37	1.10	2.27	(208) 94
	4.13	11.1	2.11	0.50	1.61	(187) 108
						Mean ~100

TABLE III. $p(I_2)=0.14$ *to* 0.16 *mm.*

$p(x)$ (mm)	$C_1\times10^{32}$ with $L=22$	with $L=10$	$p(x)$ (mm)	$C_1\times10^{32}$ with $L=22$	with $L=10$
	$X=$HYDROGEN			$X=$OXYGEN	
270	3.53	4.30	68	10.0	12.6
473	3.80	4.11	90	9.1	10.8
617	4.19	3.77	200	8.1	10.0
752	3.99	4.07	374	10.7	11.5
			563	10.5	12.0
	MEAN 4.0 ± 0.3		732	(12.8) 9.2	(16.6) 12.6
	$X=$ARGON			MEAN 10.5 ± 1.5	
90	3.67	4.05		$X=$METHANE	
120	3.44	4.00	55	11.4	14.3
226	3.20	3.60	81	9.7	9.9
373	3.66	3.62	158	14.1	10.3
556	(4.96) 3.70	3.59	382	12.5	12.6
754	(4.61) 3.35	3.42	621	14.0	14.6
	MEAN 3.6 ± 0.3			MEAN 12 ± 2	
	$X=$NITROGEN			$X=$CARBON DIOXIDE	
226	5.78	5.38	53	17.6	18.6
352	5.93	7.08	110	18.7	17.4
433	7.38	7.37	211	(24.5) 16.4	(24.9) 18.5
578	6.09	6.41	438	(29.5) 15.9	(24.7) 16.5
725	(7.82) 5.95	(10.2) 8.25	711	(35.2) 15.6	(40.8) 22.2
	MEAN 6.6 ± 1.0			MEAN 18 ± 3	

good agreement—as for instance 1.86 and 1.70 in the case of He, 10.0 and 10.7 in that of O_2, etc. The values of I (measured in μa) are expressed in Tables I and II in mm of the galvanometer (for the calculation of $\Delta I/I$) by means of a calibration factor which was determined at the beginning of each experiment (because the sensitivity of the Zernicke galvanometer is subject to variations from day to day).

Although the ΔI's are squared in the course of calculation of C_1, the results show a remarkable constancy. We have therefore assumed an accuracy of 10 to 15 percent of the mean values of C_1, obtained with the seven gases He, A, H_2, N_2, O_2, CH_4 and CO_2. Systematical deviations from the mean were often observed at the highest pressures, especially in the heavier gases. The corresponding values of C_1, are bracketed in the tables. As discussed elsewhere[7] these deviations

TABLE IV. *Velocity constants of the reaction* $I+I+X\rightarrow I_2+X \quad -d[I]/dt=C_1[I]^2[X]$.

$X=$	He	A	H_2	N_2	O_2	CH_4	CO_2	C_6H_6
$C_1\times10^{32}$	1.8	3.6	4.0	6.6	10.5	12	18	100
$C_1^*\times10^{-15}$	6.7	1.3	14.5	24	38	44	66	350
$\gamma\times10^3$	1.9	3.9	4.2	6.9	11	13	19	105

C_1, concentrations in molecules per cc.
C_1^*, same in moles per cc.

are probably due to the destruction of the thermal effect (which is caused by a *nonuniform* heating of the gas) by convection currents. The figures after the brackets give the values of C_1 calculated by neglecting the thermal correction altogether, and these values are in good agreement with the ones obtained at lower pressures. It appears as if even in the extreme case of benzene vapor no other explanation is necessary to account for the apparent increase of the C_1, values with pressure.[9] We made it plausible[7] that the convection is proportional to $pM/\kappa\eta$ (p=pressure, M=molecular weight, κ=heat conductivity, η=viscosity), and is therefore as strong in benzene vapor at $p=40$ mm as say in nitrogen at 700 mm.

In Table IV, we compare the velocity constants C_1, for all the gases investigated.

The physical meaning of the C_1 values is best revealed by the last row of Table IV, showing the proportion of the total number of double collision I+I which are "recombining collisions" at atmospheric pressure of the gas X ($t=20°$C). The number of double collisions was calculated by means of the usual kinetic formula:

$$Z=2\pi^{\frac{1}{2}}[I]^2\sigma_I^2(2RT/M)^{\frac{1}{2}}$$

using the plausible value $\sigma_I=5$A, for the collision diameter of two iodine atoms.

The γ values shown in Table IV are rather high (much higher than the usual estimate "one collision in a thousand is a triple one at atmospheric pressure"). Even in the case of helium, one collision in 530 is a recombining one; in that of carbon dioxide the porportion rises to one collision in 50, and in that of benzene vapor to one collision in ten.

[9] A possible alternative explanation is the assumption of the formation of complexes $C_6H_6\cdot I$ which combine by double collisions: $2C_6H_6I\rightarrow2C_6H_6+I_2$.

The figures in Table IV, suggest that the efficiency of gases in acting as third bodies in the recombination process is smaller in the case of monatomic gases, and greater in that of the diatomic, and polyatomic ones—obviously because the additional degrees of freedom make an energy transfer from the atom pair to the molecule an easier one. In the group of monatomic gases, as well as in that of the polyatomic ones, the efficiency generally increases with increasing size of the molecules (or with increasing intensity of van der Waals forces).[10] A more detailed discussion of this point will be attempted on a later occasion, in connection with the results obtained in an analogous investigation with bromine.[11]

Our heartiest thanks are due to Professor F. G. Donnan, F.R.S., for the possibility he gave us to work in the Sir William Ramsay Laboratories and for his kind interest in our work.

[10] It is possible that the greater influence of O_2 as compared to that of N_2 is due to the magnetic interaction of the oxygen molecule with the iodine atoms.

[11] Communicated in Trans. Faraday Soc. **32**, 907 (1936).

AUGUST, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Homogeneous Unimolecular Decomposition of Gaseous Alkyl Nitrites

VI. The Decomposition of *n*-Butyl Nitrite

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(Received April 16, 1936)

The decomposition of *n*-butyl nitrite has been investigated from 5 to 40 cm pressure in the temperature range 170 to 212°C. The reaction is homogeneous and first order. The mechanism is, in the main, the same as with the lower members of the series. The reaction is, however, complicated by the formation of condensation products and the results are therefore less accurate than those obtained with the lower members of the series. The activation energy is approximately the same as those of the other nitrites. The velocity constant at 189.9°C is 8.88×10^{-4} sec.$^{-1}$, as compared with 0.97 for methyl, 1.89 for ethyl, and 3.95 for *n*-propyl nitrite.

INTRODUCTION

IN a number of previous papers it has been shown that the thermal decompositions of the gaseous alkyl nitrites are homogeneous unimolecular reactions. All the lower members of the series appear to decompose primarily by splitting off nitric oxide and forming a free radical, *viz.*

$$RONO = RO + NO.$$

In consequence the activation energies, etc., are directly comparable for the various members of the series, and the reactions furnish an ideal opportunity to investigate the effect of chemical configuration on the reaction rate. The decompositions of methyl,[1] ethyl,[2] *n*-propyl,[3] and isopropyl[4] nitrites have already been investigated, and the present communication describes the decomposition of the next straight-chain member of the series, *n*-butyl nitrite.

[1] Steacie and Shaw, Proc. Roy. Soc. (London) **A146**, 388 (1934); Steacie and Calder, J. Chem. Phys. **4**, 96 (1936); Steacie and Rosenberg, ibid. **4**, 223 (1936).

[2] Steacie and Shaw, J. Chem. Phys. **2**, 345 (1934); Rice and Radowskas, J. Am. Chem. Soc. **56**, 214 (1935).

[3] Steacie and Shaw, J. Chem. Phys. **3**, 344 (1935).

[4] Steacie and Shaw, Proc. Roy. Soc. (London) **A151**, 685 (1935).

EXPERIMENTAL

As before reaction rates were measured by observing the rate of pressure change in a system at constant volume. On account of the higher boiling point of *n*-butyl nitrite, however,

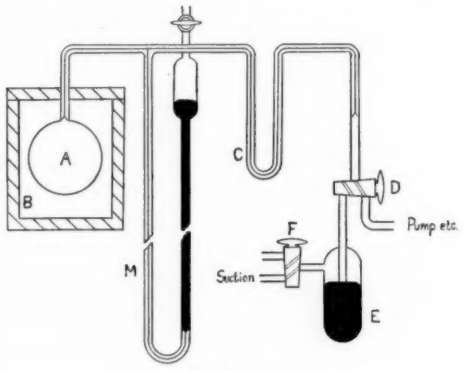

FIG. 1. Apparatus.

some modification of the apparatus previously employed was necessary. The modified portion of the apparatus is illustrated in Fig. 1.

The soft glass reaction vessel *A*, having a capacity of about 200 cc, was immersed in a well-stirred oil-bath. The temperature was determined with a thermocouple and with standard mercury thermometers. The reaction vessel was connected to a capillary manometer *M*, and through the U-tube *C* and the stopcock *D* to the pumps, nitrite supply, McLeod gauge, etc. All the connecting tubing except the bottom half of the U-tube and the last few centimeters before the tap *D* was wound with nichrome wire and heated electrically to about 115–125°C.

Prior to making an experiment, the reaction vessel was brought to the desired temperature, and the apparatus was evacuated through stopcock *D* by means of a diffusion pump. The bottom part of the U-tube *C* was then cooled with liquid air, and a roughly measured quantity of butyl nitrite was condensed into the U-tube. The two-way stopcock *D* was then turned so as to connect the reaction system to the trap *E*. By opening the tap *F* to the atmosphere mercury was forced through *D* and up the tube beyond *D* for a distance of 10 or 15 cm, and *D* was then closed. As a result *D* was completely isolated from the reaction system, and all the connecting tubing could be heated. The liquid air container was then removed from *C*, and, after a preliminary warming to −80° with solid carbon dioxide, the U-tube was surrounded with a small oil-bath heated to 125°C. The butyl nitrite in *C* evaporated almost instantaneously, and registered its pressure on the manometer *M*. The rate of the decomposition was then followed by observing the rate of pressure change in the usual way.

n-butyl nitrite was obtained from the Eastman Kodak Company. It was carefully fractionated, and the fraction boiling at 76–77.8°C was retained.

The Course of the Reaction

Inasmuch as the activation energy and the absolute rate of the decomposition were similar to those of the other nitrites, there seems to be little doubt that, as before, the primary step is the rupture of the O−NO bond,

$$C_4H_9ONO = C_4H_9O + NO.$$

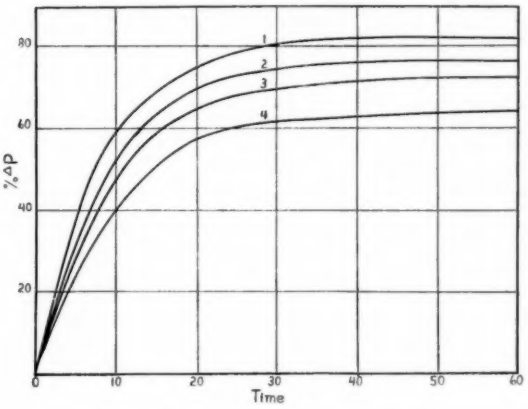

FIG. 2. Pressure increase-time curves.
Temp. = 201.8°. 1—25.6 cm; 2—18.2; 3—13.4; 4—9.5.

This would, by analogy, probably be followed by reactions leading to butyl alcohol and butyraldehyde. However, the course of the reaction was by no means as smooth as with the lower members of the series, and considerable amounts of carbon and tarry materials were deposited in the reaction bulb and connecting tubing. In view of the difficulties of analysis of such mixtures of products, and of the fact that the internal evidence completely supports the conclusion that the primary reaction is as before, no attempt has been made to determine the products of the reaction.

In previous investigations the pressure increase at the completion of the reaction was from 85 to 100 percent with various nitrites. In the present case the pressure change at completion varied considerably with the experimental conditions, as is shown by some typical pressure-time curves in Fig. 2. As a result it was no longer feasible to assume that a definite fixed pressure increase corresponded to complete reaction. All runs were therefore carried to completion, and the rate in any run was calculated from the time required for the pressure to increase 25 or 50 percent of the pressure increase at completion *in that particular run.*

The values of the pressure increase at completion are given in Table III together with the reaction rate data. It will be seen that at the higher pressures the percent pressure increase at completion is more or less independent of the temperature. At the higher temperatures, however, there is a very pronounced falling off in

TABLE I. *Typical experiments at 212.2°C.*

Initial Pressure = 24.7 cm				Initial Pressure = 6.55 cm			
Time (min.)	ΔP (cm)	% reaction	$K \times 10^3$ (sec.$^{-1}$)	Time (min.)	ΔP (cm)	% reaction	$K \times 10^3$ (sec.$^{-1}$)
1	4.0	24.6	4.69	1	1.0	28.5	4.79
2	6.8	38.2	3.99	2	1.5	43	4.69
3	9.5	53.3	4.23	3	1.9	54	4.30
4	11.4	64.0	4.25	4	2.2	63	4.10
5	12.8	72.0	4.24	5	2.5	71.5	4.23
6	13.8	77.6	4.15	6	2.75	78.5	4.25
7	14.8	83.2	4.25	7	2.9	83	4.21
8	15.4	86.5	4.17	8	3.0	86	4.10
10	16.3	91.2	3.86	9	3.15	90	4.25
12	16.5	92.6	3.61	12	3.2	91	3.41
14	17.1	96.1	3.85	15	3.3	94	4.22

TABLE II. *Typical experiments at 191.5°C.*

Initial Pressure = 24.6 cm				Initial Pressure = 5.8 cm			
Time (min.)	ΔP (cm)	% reaction	$K \times 10^4$ (sec.$^{-1}$)	Time (min.)	ΔP (cm)	% reaction	$K \times 10^4$ (sec.$^{-1}$)
2	1.7	8.1	7.01	2	0.55	9.0	7.85
4	3.8	18.1	8.25	4	1.05	17.2	7.89
6	6.3	30.0	9.90	6	1.5	24.6	7.79
8	8.5	40.5	10.79	8	1.8	29.2	7.17
10	10.1	48.0	10.90	10	2.2	36.1	7.43
12	11.15	53.1	10.48	12	2.8	45.9	8.55
15	12.6	60.0	10.19	14	3.05	50.0	8.11
20	14.55	69.3	9.48	17	3.45	56.6	8.11
30	16.75	79.8	8.88	20	4.0	65.5	8.65
35	17.55	83.5	8.59	25	4.5	73.8	8.85
40	18.15	86.5	8.50				

pressure increase at lower pressures. The fact that carbon and tarry materials are formed suggests that the lower pressure increases are to be associated with some secondary condensation reaction.

The Rate of the Reaction

Complete data for some typical experiments are given in Tables I and II. It is apparent from the tables that both at high and low pressures at 212.2° the constancy of K is quite satisfactory. At the lower temperature the constancy is still quite good at the lower pressures. At high pressures, however, K rises steadily to a maximum at about 50 percent reaction, and then falls again. This change in the form of the pressure-time curve with changing temperature may be expected to introduce some uncertainty into the calculated value of the temperature coefficient.

The summarized data for all runs are given in Table III. Runs marked P were made in a packed bulb. At the two lower temperatures it was not feasible to carry the runs to completion. It has therefore been assumed that the pressure increase at completion at these temperatures is equal to the mean value at 191.5°.

From the constancy of T_{25} and T_{50} at higher pressures it may be concluded that the reaction is definitely first order. The values of T_{25} and T_{50} vary considerably at lower pressures, however. In view of the change in the pressure increase at completion at lower pressures, it seems probable that the mechanism of the reaction is changing, and hence no great weight should be attached to the low pressure values. At higher pressures, however, the results are satisfactorily reproducible.

The runs marked P in Table III were made in a reaction vessel packed with short lengths of $\frac{1}{4}$ inch tubing. The surface/volume ratio for the packed vessel was about 6 times greater than for the empty vessel. It is apparent that no appreciable effect is produced by the increased surface. The reaction is thus homogeneous and unimolecular, and is therefore suitable for comparison with the other nitrite decompositions, although on account of its complexities we cannot expect very great accuracy in the calculated values of the velocity constant.

The Temperature Coefficient

From the foregoing discussion it is evident that only the results at the higher pressures are very trustworthy. Hence in calculating the temperature coefficient, we have used the mean values of T_{25} and T_{50} for all runs at pressures of 20 cm and over at each temperature. In Fig. 3 the logarithms of the fractional times are plotted against $1/T$. From the slopes of the lines we get 33,500 and 33,000 calories per gram mole respectively for the activation energy of the reaction.

It is apparent from the data of Tables I and II, and from similar data for all runs, that the initial rate of reaction, K_0, is equal to or slightly greater than K_{25} at high pressures and high temperatures, while at lower temperatures K_0 is considerably less than K_{25}. The result is that the temperature coefficient calculated from initial rates is somewhat higher than that calculated from T_{25} or T_{50}. It is difficult to make the extrapolation to initial rates with any certainty, but the results indicate that the true value of E

is in the neighborhood of 36,000 calories per gram mol, and hence agrees with the values previously found for the other nitrites.

On account of the uncertainty in the energy of activation, we cannot make a very direct comparison of its magnitude with that of the other members of the series, nor can we compare the values of the non-exponential factors in the expression for the rate. The safest method of procedure, therefore, is to compare the velocity constants at some arbitrarily chosen temperature. At 189.9°C, for example, we have

Substance	K, sec.$^{-1}$
Methyl nitrite	0.97×10^{-4}
Ethyl nitrite	1.89×10^{-4}
n-propyl nitrite	3.95×10^{-4}
iso-propyl nitrite	3.70×10^{-4}
n-butyl nitrite	8.88×10^{-4}

The marked regularity as we go up the series furnishes ample proof that the decomposition of butyl nitrite is strictly comparable to those of the others, and that the results have been correctly interpreted. The effect of the length of the hydrocarbon chain on the rate of reaction will be discussed in detail in a forthcoming communication.

TABLE III. *The rate of reaction.*

P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)	P_0 (cm)	Final % ΔP	T_{25} (sec.)	T_{50} (sec.)
Temperature = 212.2°C							
32.8	80	72	166	15.3	65	70	161
31.8	82	73	171	10.9	62	71	190
24.6	72	63	166	10.3	56	55	164
23.3	72	70	160	6.5	54	54	156
23.2	77	70	177	5.4	57	47	143
23.0	75	66	171	3.7	49	45	114
19.9	61	70	180	3.7	53	45	145
19.2	66	72	139	40.2*P*	83	81	158
18.0	67	72	180	34.3*P*	79	64	138
16.3	63	70	185	26.0*P*	73	80	175
16.0	64	70	163				
Temperature = 201.8°C							
33.3	73	171	317	13.6	77	183	414
32.0	82	153	296	13.4	73	176	396
29.0	76	158	315	13.3	69	195	405
27.8	78	120	310	9.3	57	183	500
25.7	75	166	330	9.2	65	155	395
25.6	83	168	340	8.8	58	201	428
25.0	80	167	316	8.5	67	177	465
24.7	72	137	330	8.4	62	220	525
22.3	73	185	354	7.2	65	188	520
21.5	79	168	323	6.7	65	158	403
19.6	73	166	363	38.3*P*	86	140	287
19.6	75	172	300	28.5*P*	80	176	339
18.2	78	177	402	20.7*P*	78	183	390
17.5	76	191	398	8.0*P*	67	248	464
15.8	66	216	450				
Temperature = 191.5°C							
43.2	82	253	740	18.8	76	347	690
33.7	77	260	600	17.8	78	347	675
29.8	82	274	669	14.8	78	347	675
28.6	79	300	640	8.3	75	458	960
25.6	85	300	660	5.5	65	444	1080
24.6	85	305	636	32.6*P*	80	330	660
23.7	79	303	600	25.2*P*	—	300	720
20.9	82	330	642				
Temperature = 181.3°C							
37.3	—	534	1770	5.8	—	1040	2115
29.2	—	612	1800	42.2*P*	—	640	1680
24.8	—	612	1775	35.5*P*	—	580	1500
22.1	—	640	1660	23.8*P*	—	640	1620
Temperature = 170.5°C							
35.3	—	1860	5640	22.1	—	1860	5460
25.2	—	1908	—	28.5*P*	—	1882	4980

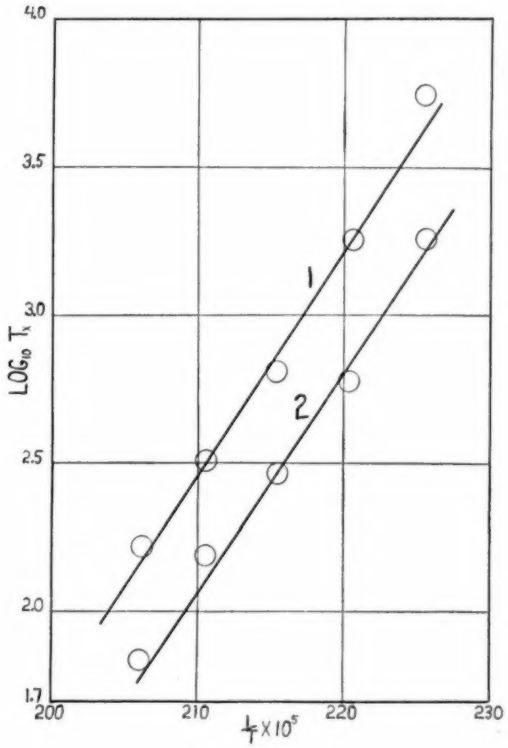

FIG. 3. Temperature coefficient.
1—T_{50}; 2—T_{25}.

The Normal Vibrations and the Isotope Effect of Molecules of the Type X_2Y_N with an N-Fold Axis of Symmetry

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(Received June 13, 1936)

In the present study it is assumed that the Y atoms are at the corners of a regular polygon and the X atoms are symmetrically situated on the N-fold axis of symmetry. The frequencies are calculated in terms of the parameters of a general quadratic potential energy form, the masses, and the geometrical constants of the figure. Frequency shifts due to isotopes are also calculated.

INTRODUCTION

THE general aspects of the theory of normal vibrations of polyatomic molecules have been treated by Brester,[1] Wigner,[2] Dennison,[3] Tisza,[4] and Wilson.[5] Other workers[6, 7, 8, 9] have given specific treatments for molecules of the form XY_2, XYZ, XY_3, XY_4 which included the derivation of algebraic expressions for the values of the frequencies and studies of the isotope effect. In the present paper this work is continued and a symmetrical molecule of the form X_2Y_N is investigated. The expression used for the potential energy is the most general consistent with the symmetry. By a series of transformations which take full advantage of the symmetry, the kinetic energy and the potential energy matrices are brought to the diagonal form. The values of the frequencies and the shifts due to isotopes are then calculated. In order to enable one to see more clearly and briefly which calculations to make, matrix notation is introduced.

GENERAL THEORY

Let there be n particles in equilibrium to which are ascribed $3n$ coordinates whose equilibrium values are $X_1, X_2, X_3, \cdots, X_{3n}$. Let the corresponding displacements $x_1, x_2, x_3, \cdots, x_{3n}$ be written in the form of a column so as to constitute a $3n$-row, 1-column matrix which will be denoted by x. Let $\mathbf{x}$ denote the transposed matrix. The usual expressions for the potential and kinetic energies

$$2V=\sum\sum v_{jk}x_jx_k, \qquad 2T=\sum\sum t_{jk}\dot{x}_j\dot{x}_k \tag{1}$$

can be written in matrix notation as follows

$$2V=\mathbf{x}v_xx, \qquad 2T=\dot{\mathbf{x}}t_x\dot{x}, \tag{2}$$

where $v_x=\|v_{jk}\|$ and $t_x=\|t_{jk}\|$. v_x and t_x will be called the potential and kinetic energy matrices respectively. When one transforms to a new set of coordinates y in accordance with the transformation $x=S_x{}^yy$ where $S_x{}^y$ is a matrix constant in time, then it can be seen that v_x, t_x, $t_x{}^{-1}$ transform according to the following equations

$$v_y=\mathbf{S}_x{}^yv_xS_x{}^y, \quad t_y=\mathbf{S}_x{}^yt_xS_x{}^y, \quad t_y{}^{-1}=S_y{}^xt_x{}^{-1}\mathbf{S}_y{}^x. \tag{3}$$

According to a well-known theorem[10] the normal frequencies of vibration ν_j are given by $4\pi^2\nu_j{}^2=\lambda_j$ where the λ_j are roots of the following equation

$$|\lambda t_x-v_x|=0. \tag{4}$$

In the present paper the derived form

$$|\lambda 1-t_x{}^{-1}v_x|=0 \tag{5}$$

will be used instead of Eq. 4.

If some of the x coordinates are complex and moreover the complex coordinates occur in conjugate pairs then it can be shown that Eqs. (2), (3), (4), (5) are still valid if $\mathbf{x}$ is reinterpreted as the transposed conjugate complex to x. Under this new interpretation the previous equations for real coordinates are a special case of the more general equations for complex coordinates.

[1] C. J. Brester, *Kristall-symmetrie und Reststrahlen*, Dissertation, Utrecht (1923).
[2] E. Wigner, Goettinger Nachr. Math. Phys. Klasse (1930) p. 133.
[3] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[4] L. Tisza, Zeits. f. Physik **82**, 48 (1933).
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[6] Salant and Rosenthal, Phys. Rev. **42**, 812 (1932).
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[8] Adel, Phys. Rev. **45**, 56 (1934).
[9] J. Rosenthal, Phys. Rev. **45**, 538 (1934).

[10] See for example reference 3, p. 284.

The Geometric Model and the Coordinates

It is assumed that the N similar Y atoms are located at the vertices of a regular polygon. The two X atoms are situated on the N-fold axis of symmetry, equidistant from the plane of the regular polygon. The Y atoms are labelled by the subscripts $0, 1, 2, \cdots, N-1$. One of the X atoms is labelled by a superscript prime, the other by a superscript double prime. The radius of the circumscribed circle of the regular polygon is denoted by R. The ratio of the distance between the two X atoms to the radius R is denoted by $2h$. The geometric model is illustrated in Fig. 1 for the case $N=3$. In this figure the atoms are labelled by their respective masses. Note the relations $m'=m''$, $m_j=m$, $j=0, 1, 2, \cdots, N-1$. A number of sets of displacement coordinates are used. Throughout subsequent calculations these displacements are considered mathematically infinitesimal and higher order terms are neglected. This is the usual approximation made in work of this type.

x or cartesian coordinates

A system of cartesian coordinates at rest are used for the initial expression of the kinetic energy. The z axis is the N-fold axis of symmetry of the equilibrium configuration. The x axis passes through the equilibrium position of m_0. The equilibrium values of the coordinates are given by the following equations

$$X_j=R\,\mathrm{Cos}\,j\theta, \quad Y_j=R\,\mathrm{Sin}\,j\theta, \quad \theta=2\pi/N, \tag{6}$$
$$Z'=-Z''=hR, \quad Z_j=X'=X''=Y'=Y''=0.$$

The displacements are denoted by corresponding small letters. The whole set of displacements will be represented by the matrix x.

p coordinates

The following $3N$ interatomic distances are convenient for the initial expression of the potential energy

$P_j'+p_j'$ the distance from m_j to m',
$P_j''+p_j''$ the distance from m_j to m'',
Q_j+q_j the distance from m_j to m_{j+1}.

Again equilibrium values are denoted by capital letters and displacements by small letters. Note the relations

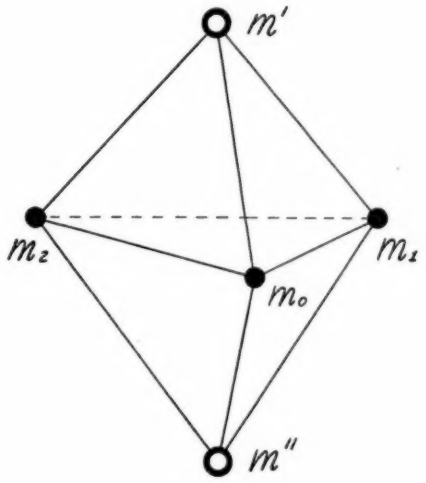

Fig. 1.

$$P_j'=P_j''=P=R(1+h^2)^{\frac{1}{2}},$$
$$Q_j=Q=2R\,\mathrm{Sin}\,\theta/2, \quad j=0, 1, 2, \cdots, N-1. \tag{7}$$

To complete the set p the following six coordinates α_x, α_y, α_z, β_x, β_y, β_z are added. Note that the definitions of α_y, α_z, β_y, β_z are analogous to those of α_x, β_x.

$$\alpha_x=\sum_j m_j x_j+m'x'+m''x'',$$
$$\beta_x=\sum_j m_j(Y_jz_j-Z_jy_j)+m'(Y'z'-Z'y') \tag{8}$$
$$+m''(Y''z''-Z''y'').$$

The time derivatives of these six coordinates are equal to the six components of linear and angular momentum. The six coordinates are therefore constants, in particular zero.

ϕ coordinates

These symmetry coordinates were chosen because v_ϕ and t_ϕ^{-1} could be shown to have an almost diagonal form, and are defined as follows:

$$\phi_j'=\sum_k \epsilon^{jk}(p_k'-p_k'')N^{-\frac{1}{2}}P/2R,$$
$$\phi_j''=\sum_k \epsilon^{jk}(p_k'+p_k'')N^{-\frac{1}{2}}P/2R,$$
$$\phi_j'''=\sum \epsilon^{j(k+\frac{1}{2})}q_kN^{-\frac{1}{2}}Q/R. \tag{9}$$

ϵ denotes the primitive Nth root of unity.

In order to make the transformation from x to ϕ coordinates an initial transformation from x to p coordinates is made. This initial transformation

is given by the following first order equations which may be readily derived from the geometry of the figure:

$$\begin{aligned} Pp_j' &= X_j(x_j-x') + Y_j(y_j-y') \\ &\qquad -Z'(z_j-z'), \\ Pp_j'' &= X_j(x_j-x'') + Y_j(y_j-y'') \\ &\qquad -Z''(z_j-z''), \\ Qq_j &= (X_{j+1}-X_j)(x_{j+1}-x_j) \\ &\qquad +(Y_{j+1}-Y_j)(y_{j+1}-y_j). \end{aligned} \tag{10}$$

n or normal coordinates

These coordinates are defined by the property that the kinetic energy matrix is unity and the potential energy matrix is diagonal. Their significance is well known and their calculation is postponed pending the calculation of the frequencies.

The Potential Energy Matrix

Since the potential energy is independent of the six degrees of freedom corresponding to rotation and translation, it may be expressed in terms of the $3N$ coordinates p_j', p_j'', q_j or ϕ_j', ϕ_j'', ϕ_j'''. The forms of the matrices v_p and v_ϕ were investigated by performing the following three symmetrical operations:

(1) Reflection with respect to the x, y plane

$p_j' \to p_j''$, $p_j'' \to p_j'$, $q_j \to q_j$,
$\phi_j' \to -\phi_j'$, $\phi_j'' \to \phi_j''$, $\phi_j''' \to \phi_j'''$.

(2) Rotation about the z axis by an angle $\theta = 2\pi/N$

$p_j' \to p_{j+1}'$, $p_j'' \to p_{j+1}''$, $q_j \to q_{j+1}$,
$\phi_j' \to \epsilon^{-j}\phi_j'$, $\phi_j'' \to \epsilon^{-j}\phi_j''$, $\phi_j''' \to \epsilon^{-j}\phi_j'''$.

(3) Reflection with respect to the x, z plane

$p_j' \to p_{N-j}'$, $p_j'' \to p_{N-j}''$, $q_j \to q_{N-j-1}$,
$\phi_j' \to \phi_{N-j}'$, $\phi_j'' \to \phi_{N-j}''$, $\phi_j''' \to -\phi_{N-j}'''$.

The action of the symmetrical operations upon the coordinates p_j', p_j'', q_j and ϕ_j', ϕ_j'', ϕ_j''' is indicated in order to show how one takes into account symmetry. It is clear that after any one of the three operations the geometric figure and the potential and kinetic energy matrices will retain their original form. Consider the following examples of this method applied to the investigation of v_ϕ.

As a consequence of operation (1) $\phi_j'\phi_k'' \to -\phi_j'\phi_k''$. The coefficient of $\phi_j'\phi_k''$ must be zero in order for v_ϕ to remain unaltered after this symmetrical operation.

As a consequence of operation (2) $\phi_j'\phi_k' \to \epsilon^{-j-k}\phi_j'\phi_k'$ so that only the coefficient of $\phi_j'\phi_{N-j}'$ may be non-vanishing and v_ϕ retain its original form.

As a consequence of operation (3) $\phi_j''\phi_{N-j}''' \to -\phi_{N-j}''\phi_j'''$ and $\phi_{N-j}''\phi_j''' \to -\phi_j''\phi_{N-j}'''$. In order for v_ϕ to remain unaltered the coefficients of the terms $\phi_j''\phi_{N-j}'''$, $\phi_{N-j}''\phi_j'''$ must be opposite in sign.

In order to present the results of the above considerations it is convenient to group the ϕ coordinates into the submatrices ϕ', ϕ'', ϕ''', α, β. They are defined as follows:

$$\phi' = \begin{pmatrix} \phi_0' \\ \phi_1' \\ \cdot \\ \cdot \\ \cdot \\ \phi_{N-1}' \end{pmatrix}, \quad \phi'' = \begin{pmatrix} \phi_0'' \\ \phi_1'' \\ \cdot \\ \cdot \\ \cdot \\ \phi_{N-1}'' \end{pmatrix}, \quad \phi''' = \begin{pmatrix} \phi_0''' \\ \phi_1''' \\ \cdot \\ \cdot \\ \cdot \\ \phi_{N-1}''' \end{pmatrix},$$

$$\alpha = \begin{pmatrix} \alpha_x \\ \alpha_y \\ \alpha_z \end{pmatrix}, \quad \beta = \begin{pmatrix} \beta_x \\ \beta_y \\ \beta_z \end{pmatrix}.$$

The submatrices of the p coordinates, namely p', p'', q, α, β are defined analogously.

By means of the considerations previously illustrated it can be shown that v_p and v_ϕ have the following forms:

v_p	$\mathbf{p'}$	$\mathbf{p''}$	$\mathbf{q}$	$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$
p'	a'	b'	c'	0	0
p''	$\mathbf{b'}$	a'	c'	0	0
q	$\mathbf{c'}$	$\mathbf{c'}$	d'	0	0
α	0	0	0	0	0
β	0	0	0	0	0

v_ϕ	$\boldsymbol{\phi'}$	$\boldsymbol{\phi''}$	$\boldsymbol{\phi'''}$	$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$
ϕ'	a	0	0	0	0
ϕ''	0	b	c	0	0
ϕ'''	0	c	d	0	0
α	0	0	0	0	0
β	0	0	0	0	0

a' b' c' d' are non-diagonal submatrices while a, b, c, d are diagonal submatrices. The following equations relate the elements of v_p and v_ϕ.

$$\begin{aligned} a_{jj} &= 2R^2/P^2 \sum_k (a_{0k}' - b_{0k}') \cos jk\theta, \\ b_{jj} &= 2R^2/P^2 \sum_k (a_{0k}' + b_{0k}') \cos jk\theta, \\ c_{jj} &= 2R^2/PQ \sum_k c_{0k}' \cos j(k+\tfrac{1}{2})\theta, \\ d_{jj} &= R^2/Q^2 \sum_k d_{0k}' \cos jk\theta. \end{aligned} \tag{11}$$

The Kinetic Energy Matrix

It is to be expected that the kinetic energy matrix and its reciprocal will have simple forms

for the ϕ coordinates. t_ϕ^{-1} can be calculated by using Eq. (3); namely $t_\phi^{-1}=S_\phi{}^x t_x^{-1}\mathbf{S}_\phi{}^x$ and is found to have the following form:

t_ϕ^{-1}	ϕ'	ϕ''	ϕ'''	α	β
ϕ'	A	0	0	0	0
ϕ''	0	B	C	0	0
ϕ'''	0	C	D	0	0
α	0	0	0	M_α	0
β	0	0	0	0	I_β

The submatrices A, B, C, D, M_α, M_β are all diagonal. In particular

$$M_\alpha=\begin{Vmatrix} M & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & M \end{Vmatrix}, \quad I_\beta=\begin{Vmatrix} I_x & 0 & 0 \\ 0 & I_y & 0 \\ 0 & 0 & I_z \end{Vmatrix},$$

where M is the total mass of all the atoms and I_x, I_y, I_z are the moments of inertia about the three axes. The following are the values of the diagonal terms of the other submatrices. The reciprocals of the masses m, m' are denoted by μ, μ', respectively.

$$\begin{aligned} &A_0=h^2\mu+h^2\mu' N/2, \quad A_1=A_{N-1}=h^2\mu+\mu' N/4, \\ &\qquad A_j=A_{N-j}=h^2\mu. \quad 1<j\leq N/2, \\ &B_0=\mu+h^2\mu' N/2, \quad B_1=B_{N-1}=\mu+\mu' N/4, \\ &\qquad B_j=B_{N-j}=\mu, \quad 1<j\leq N/2, \\ &C_j=2(1-\cos\theta)\ \mathrm{Cos}\,[j\theta/2]\mu, \\ &D_j=4(1-\cos\theta)^2\ \mathrm{Cos}^2\,[j\theta/2]\mu \\ &\qquad +4\ \mathrm{Sin}^2\,\theta\ \mathrm{Sin}^2\,[j\theta/2]\mu. \end{aligned} \tag{12}$$

The Values of the Frequencies

The values of λ can be obtained by solving $|\lambda 1-t_\phi^{-1}v_\phi|=0$ after utilizing the values just obtained for t_ϕ^{-1}, v_ϕ. The following linear and quadratic equations give the values of λ:

$$\begin{aligned} &\lambda_j'=A_j a_j, \quad \lambda_j''+\lambda_j'''=B_j b_j+2C_j c_j+D_j d_j, \\ &\qquad \lambda''\lambda'''=[B_j D_j-C_j^2][b_j d_j-c_j^2]. \end{aligned} \tag{13}$$

Most of the frequencies are double as shown by the relations:

$$\lambda_j'=\lambda_{N-j}', \quad \lambda_j''=\lambda_{N-j}'', \quad \lambda_j'''=\lambda_{N-j}''', \quad 0<j<N.$$

The Normal Coordinates and the Normal Vibrations

The normal coordinates n may be determined from the following equations:

$$\lambda=v_n=\mathbf{S}_\phi{}^n v_\phi S_\phi{}^n, \quad 1=t_n{}^{-1}=S_n{}^\phi t_\phi{}^{-1}\mathbf{S}_n{}^\phi. \tag{14}$$

From these equations the following expressions for n may be derived:

$$\begin{aligned} &0<j<N/2, \quad n_j'+in_{N-j}''=\gamma_{11,\,j}\phi_j'\sqrt{2}, \\ &n_j''+in_{N-j}''=[\gamma_{22,\,j}\phi_j''+\gamma_{23,\,j}\phi_j''']\sqrt{2}, \\ &n_j'''+in_{N-j}'''=[\gamma_{32,\,j}\phi_j''+\gamma_{33,\,j}\phi_j''']\sqrt{2}. \end{aligned} \tag{15}$$

It is to be noted that these expressions are not accurate for the cases $j=0$, $j=N/2$. In the latter cases the complex term is to be omitted from the left-hand side of the equation and the factor $\sqrt{2}$ from the right side of the equation. The constants introduced in Eqs. (15) have the following values:

$$\begin{aligned} &\gamma_j=[B_j D_j-C_j^2], \quad \gamma_{11,\,j}=[A_j]^{-\frac{1}{2}}, \\ &\gamma_{22,\,j}=[\gamma_j b_j-D_j\lambda_j''']^{\frac{1}{2}}[\gamma_j(\lambda_j''-\lambda_j''')]^{-\frac{1}{2}}, \\ &\gamma_{23,\,j}=[\gamma_j d_j-B_j\lambda_j''']^{\frac{1}{2}}[\gamma_j(\lambda_j'''-\lambda_j'')]^{-\frac{1}{2}}, \\ &\gamma_{32,\,j}=[\gamma_j b_j-D_j\lambda_j'']^{\frac{1}{2}}[\gamma_j(\lambda_j''-\lambda_j''')]^{-\frac{1}{2}}, \\ &\gamma_{33,\,j}=[\gamma_j d_j-B_j\lambda_j'']^{\frac{1}{2}}[\gamma_j(\lambda_j'''-\lambda_j'')]^{-\frac{1}{2}}. \end{aligned} \tag{16}$$

Now that the normal coordinates have been obtained one can solve for the complete transformation $S_x{}^n$ from n to x coordinates. $S_x{}^n$ gives the complete geometrical representation of the normal vibrations. Its explicit form is rather long and complex and will be omitted. One may derive from it the following qualitative results.

The vibration λ_0' is active with electrical moment parallel to the axis of symmetry; the

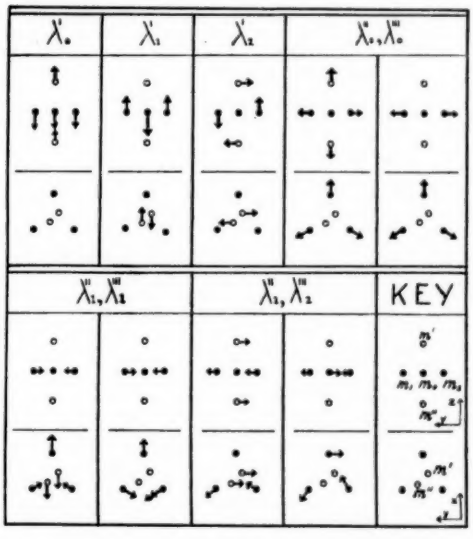

FIG. 2.

vibrations λ_1'', λ_1''', λ_{N-1}'', λ_{N-1}''' are active with electrical moment perpendicular to the axis of symmetry; the remaining vibrations are inactive.

The complete results are graphically illustrated for the molecule X_2Y_3 by Fig. 2.

The Isotope Effect

The effects due to the presence of an isotope of either one X atom or one Y atom or the simultaneous presence of both will now be considered. Let the symbol corresponding to the variation in any particular quantity be denoted by a prefixed δ and in particular let the variations of the reciprocals of the masses of the two isotopic atoms be $(\delta\mu_0)$, $(\delta\mu')$. The usual assumption will be made that v_p is not affected by the presence of isotopes. Calculation of t_ϕ^{-1} and careful examination of its subsequent usage indicates that only the variations in the elements that were previously nonzero affect the final results. The values of the following variations in the elements of t_ϕ^{-1} were obtained by recalculating t_ϕ^{-1} according to the method already presented.

$$
\begin{aligned}
&(\delta A_0)=(\delta\mu_0)h^2/N+(\delta\mu')h^2N/4,\ (\delta A_{N/2})=(\delta\mu_0)h^2/N,\ (\delta A_j)=(\delta\mu_0)2h^2/N,\ (\delta A_{N-j})=0,\ 1<j<N/2,\\
&(\delta A_1)=(\delta\mu_0)2h^2/N+(\delta\mu')N/8,\ (\delta A_{N-1})=(\delta\mu')N/8,\ (\delta B_1)=(\delta\mu_0)2/N+(\delta\mu')N/8,\ (\delta B_{N-1})=(\delta\mu')N/8,\\
&(\delta B_0)=(\delta\mu_0)/N+(\delta\mu')h^2N/4,\ \ (\delta B_{N/2})=(\delta\mu_0)/N,\ \ (\delta B_j)=(\delta\mu_0)2/N,\ \ \delta B_{N-j}=0,\ \ 1<j<N/2,\\
&(\delta C_0)=(\delta\mu_0)2(1-\cos\theta)/N,\ (\delta C_{N/2})=0,\ (\delta C_j)=(\delta\mu_0)4(1-\cos\theta)\cos[j\theta/2]/N,\ (\delta C_{N-j})=0,\ 0<j<N/2,\\
&(\delta D_0)=(\delta\mu_0)4(1-\cos\theta)^2/N,\quad (\delta D_{N/2})=(\delta\mu_0)4\sin^2\theta/N,\\
&(\delta D_j)=(\delta\mu_0)8(1-\cos\theta)^2\cos^2[j\theta/2]/N,\quad \delta D_{N-j}=(\delta\mu_0)8\sin^2\theta\sin^2[j\theta/2]/N,\quad 0<j<N/2. \qquad (17)
\end{aligned}
$$

The values of $(\delta\lambda)$ may be derived by observing the variations in the expressions for λ given by Eqs. (13). The following results are obtained:

$$
\begin{aligned}
&(\delta\lambda_j')/\lambda_j'=(\delta A_j)/A_j,\\
&(\delta\lambda_j'')+(\delta\lambda_j''')=b_j(\delta B_j)+2c_j(\delta C_j)+d_j(\delta D_j),\\
&(\delta\lambda_j'')/\lambda_j''+(\delta\lambda_j''')/\lambda_j'''=[D_j(\delta B_j)\\
&\qquad +B_j(\delta D_j)-2C_j(\delta C_j)]/[B_jD_j-C_j^2]. \qquad (18)
\end{aligned}
$$

Due to the presence of isotopes a new set of normal coordinates n' will be required. The following are the fundamental equations for the new coordinates:

$$
\begin{aligned}
&v_{n'}=\lambda+(\delta\lambda)=\mathbf{S}_n{}^{n'}v_nS_n{}^{n'},\\
&1=t_{n'}{}^{-1}=S_{n'}{}^x[t_x{}^{-1}+(\delta t_x{}^{-1})]\mathbf{S}_{n'}{}^x\\
&\qquad =S_{n'}{}^nS_n{}^x[t_x{}^{-1}+(\delta t_x{}^{-1})]\mathbf{S}_n{}^x\mathbf{S}_{n'}{}^n. \qquad (19)
\end{aligned}
$$

By making first order approximations the transformation $S_{n'}{}^n$ which expresses the new normal coordinates in terms of the old may be calculated. By utilizing this result one obtains the complete qualitative description of the isotope effect now given.

Effects due to isotope of X atom

All frequencies that were double remain so. The following frequencies shift in value. They are also the only active frequencies. λ_0', λ_0'', λ_0''' have ($\|$) moments. λ_1', λ_1'', λ_1''', λ_{N-1}', λ_{N-1}'', λ_{N-1}''' have ($\perp$) moments.

Effects due to isotope of Y atom

All frequencies become single. All frequencies with the exception of λ_j' $j>N/2$ are active and shift in value. λ_j', $j\leq N/2$ have ($\|$) moments. λ_j'' and λ_j''' have ($\perp$) moments.

Concluding Remarks

The coordinates used lend themselves readily to the introduction of various force models. Although preliminary calculations of a number of force models have been carried out, the author felt that such calculations should go hand in hand with the examination of experimental data, and accordingly has omitted these calculations, inasmuch as experimental data have not been treated in the present paper. The writer wishes to express sincere thanks to Professor E. E. Witmer for his guidance in solving the problem presented in this paper.

Transfer of Rotational Energy in Molecular Collisions

I. Elementary Processes Which Lead to Abnormal Rotation of the HgH Molecule*

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By the application of photographic photometry, the intensity distribution within the HgH 4017 band excited by mercury-sensitized fluorescence has been studied as a function of the pressure of nitrogen and the pressure of water vapor present in the fluorescence tube. From the effect which the foreign gases exert on the observed distribution of molecules among rotational levels, conclusions are drawn regarding the transfers of energy which occur in collisions of the HgH molecule with metastable Hg atoms and with normal H_2O and N_2 molecules. The proportion of excited HgH molecules with rotational energy greater than 0.2 volt greatly exceeds the thermal value under all circumstances; the excess rotational energy has its source in the two following processes. In a collision between an unexcited HgH molecule and a metastable Hg atom, the excitation energy of the latter is sometimes taken up as both rotational and electronic energy of the HgH molecule. In a collision between a normal N_2 molecule and a highly excited HgH molecule, part of the electronic and vibrational energy of the latter is converted into rotational energy.

I. INTRODUCTION

IN many cases the "rotational temperature" derived from the intensity distribution in an emission band of a molecule is not at all related to the temperature of the light source. This abnormality was first observed by Gaviola and Wood[1] in the spectrum of HgH excited by mercury-sensitized fluorescence. The intensity distribution may correspond to a temperature of thousands of degrees even though the light source operates at room temperature. The phenomenon has been interpreted in two different ways,[2, 3, 4] leading to contradictory conclusions regarding the effects of various elementary processes—in particular, collisions—on the rotation of the HgH molecule.

Processes representing exchanges of energy in collisions play an ever increasing part in theories of chemical reactions. For example in the discussion of the energy chains by Semenoff in his recent book *Chemical Kinetics and Chain Reactions*,[5] it is frequently assumed that energy of formation is largely retained by a molecule through many collisions so that it remains available as energy of activation in a subsequent reaction. The relationship of intermolecular transfers of energy to abnormal intensity distributions in band spectra has been reviewed by Oldenberg.[6]

The present experiments on the sensitized fluorescence of HgH were undertaken in an attempt to discriminate between the two theories mentioned above, and to obtain additional information about intermolecular transfers of energy, particularly those involving rotation. Preliminary reports on various aspects of the problem have been published.[7]

II. PREVIOUS WORK

Gaviola and Wood[1] discovered that the HgH spectrum could be excited in sensitized fluorescence under two different conditions: The fluorescence tube might contain, in addition to a small amount of mercury vapor (about 0.001 mm), either (A) a few thousandths of a mm of H_2 plus a few mm of N_2, or (B) a few mm of water vapor. They pointed out that both sets of conditions are favorable for the production of a high concentration of metastable Hg atoms, for both H_2O and N_2 molecules are very effective in transferring Hg atoms from the 6^3P_1 state to the metastable 6^3P_0 state. In case A the high rotation lines were very intense as shown by the marked tails on the individual bands; but in B the tails of the bands were relatively weak and the heads

* This paper is in part an extract from a thesis presented for the degree of Doctor of Philosophy.

[1] E. Gaviola and R. W. Wood, Phil. Mag. (7) **6**, 1191 (1928).

[2] H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie **B8**, 403 (1930).

[3] O. Oldenberg, Phys. Rev. **37**, 194 (1931).

[4] O. Oldenberg, Phys. Rev. **37**, 1550 (1931).

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[6] O. Oldenberg, Phys. Rev. **46**, 210 (1934).

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pronounced, indicating a predominance of the low rotation lines. They inferred from this difference in intensity distribution that the excited HgH molecule might lose rotation in a collision with an H_2O molecule, but not in a collision with an N_2 molecule.

Beutler and Rabinowitch[2] repeated the experiments and compared the spectra with schematic bands computed for rotational temperatures of 3000°K and 300°K. They concluded that the former temperature corresponded to case A, the latter to case B. They pointed out that if, as suggested by Gaviola and Wood, the low rotation for case B were caused by loss of rotation by excited HgH molecules in collisions with H_2O molecules, the rotational temperature should depend on the pressure of water vapor; nevertheless they found always the same intensity distribution when the experiments were performed with water vapor pressures varying from 0.5 to 12 mm. Because of this contradiction, as well as objections to other processes suggested by Gaviola and Wood, they undertook a re-examination of the reactions of excited Hg atoms with N_2, H_2, and H_2O molecules.

After detailed considerations, Beutler and Rabinowitch concluded that the occurrence of the bands is to be explained by the following elementary processes. The HgH molecule is formed in an exchange reaction:

$$Hg(6^3P_0)+H_2\rightarrow HgH+H+0.62 \text{ volt}, \quad (1a)$$

$$Hg(6^3P_0)+H_2O\rightarrow HgH+OH-0.1 \text{ volt}. \quad (1b)$$

The resulting HgH molecule is in the normal electronic state and receives the excitation energy necessary for the emission of the bands in a subsequent collision of the second kind:

$$Hg(6^3P_0)+HgH\rightarrow Hg(6^1S_0)+HgH', \quad (2)$$

which is followed by a radiation process:

$$HgH'\rightarrow HgH+h\nu. \quad (3)$$

The difference in intensity distribution for cases A and B is explained on the basis of the energy relations in processes (1a) and (1b). In (1b) the energy deficiency, which must be made up from thermal energy of the reacting molecules, precludes any excess energy of rotation. Process (1a) provides ample energy and fulfills other conditions[8] for the production of a HgH molecule with high energy of rotation. However, if the excess rotation produced in this way is to manifest itself in the emission spectrum, it must persist during the time intervening between processes (1a) and (2). Inasmuch as the concentration of $Hg6^3P_0$ atoms is of the order of 10^{-5} that of the N_2 molecules, many thousands of collisions with the latter will occur in this interval. Beutler and Rabinowitch concluded that the very high rotational temperature observed for case A is evidence that at least a considerable fraction of the rotation set up in the reaction (2a) actually does persist through thousands of collisions.

Oldenberg[3] has offered an alternative interpretation which retains the elementary processes suggested by Beutler and Rabinowitch but explains the peculiarities in the intensity distributions without the assumption of an extreme persistence of rotation. He assumes that whether or not abnormal rotation is produced in the formation processes is unimportant, but that the abnormal rotation exhibited by the emission spectrum arises principally in the excitation process and in collisions during the lifetime of the excited molecule. Those assumptions are supported by tentative general rules relating to transfers of energy which he has derived by application of classical mechanics to molecular collisions. It is anticipated that classical mechanics may give an approximate description of the motions of the atomic nuclei in molecular collisions, just as it affords a derivation of the Franck-Condon rule for vibrational transitions in a molecule. His starting point is the familiar fact that in a collision between two particles kinetic energy is readily exchanged only in case the particles are of nearly equal masses; if the masses are very different the exchange of energy is small, but the direction of motion of the lighter particle may be altered. Accordingly, in a molecular collision kinetic energy of rotation or vibration associated with the motion of any atom within a molecule should be transferred in appreciable amounts to an atom of a second molecule (or to a free atom) only in case the atoms are of nearly equal mass.

The above ideas lead to the following conclusions: In a collision between HgH and N_2 mole-

[8] H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie **B8**, 231 (1930).

cules, rotational energy of the HgH, localized almost entirely in the light H atom, can be transferred only in small amounts to any degree of freedom of the N_2 molecule; but energy of vibration can be transformed into energy of rotation of the same HgH molecule. The H_2O molecule does contain light atoms; thus in a collision it should be able to rob the HgH molecule of any excess vibrational and rotational energy. An extension of the Franck-Condon principle to collisions of the second kind indicates that process 3 can lead to an excited HgH molecule with high vibration. It is possible that the presence of the free Hg atom at the instant of excitation can result in transfer of the vibration into rotation.[4] In case A, the few collisions with N_2 molecules which occur during the lifetime of the excited state of the HgH might also lead to transfer of vibration into rotation, but not to appreciable loss of rotation. The high rotation observed in case A is thus explained. Collisions with H_2O molecules should lead to dissipation of both vibration and rotation, resulting in a spectrum with approximately normal rotation, as is observed for case B.

III. Program

Either of the interpretations—one by Beutler and Rabinowitch, the other by Oldenberg—is consistent with the simple observations outlined above. Since those observations consist of estimates of rotational temperature based on mere inspection of photographic plates, it seemed desirable that the experiments be repeated with objective intensity measurements. Furthermore, it appeared that certain additional experiments would add considerably to the information to be obtained; accordingly a systematic investigation of the intensity distribution of the HgH bands excited by sensitized fluorescence was undertaken.

Measurements of intensity distributions were made by methods of photographic photometry. The relation between the intensity distribution and the pressure of nitrogen for case A, and the pressure of water vapor for case B, was investigated thoroughly. Additional experiments were performed with various mixtures of nitrogen and water vapor in the fluorescence tube (hereafter referred to as case C), since they gave some promise of discriminating between the two explanations of the difference in the intensity distribution for cases A and B. In this case C it is to be expected that the HgH molecules are formed in reaction (1b) and consequently should start with the same amount of rotational energy as in case B. If the rotation is very little influenced by the excitation process and subsequent collisions with N_2, as assumed by Beutler and Rabinowitch, the intensity distribution in the bands should be the same as for case B. If, on the other hand, the excitation process and collisions with nitrogen during the lifetime of the excited state result in increased rotational energy, as suggested by Oldenberg, abnormal rotation should be observed, as in case A.

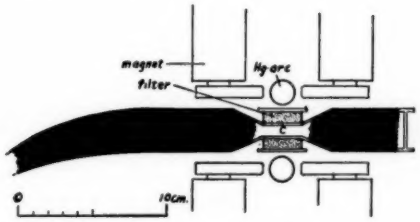

FIG. 1. Quartz fluorescence tube. The fluorescence occurs in the region *C*. The tube is flattened at *C* (cross section 8 mm×30 mm) in order to reduce the absorbing layer of Hg vapor between the arcs and the central section of the tube.

IV. Apparatus

The quartz fluorescence tube is illustrated in Fig. 1. It was designed to make possible very intense illumination, thus taking advantage of the fact that the intensity of the HgH bands is proportional to the square of the intensity of the exciting light, as discovered by Gaviola and Wood. The fluorescence occurs in the region *C*; the rectangular constriction (cross section 8 mm × 30 mm) at that part of the tube has the purpose of reducing the absorbing layer of mercury vapor through which the exciting radiation must pass before it reaches the center of the tube.

In order to reduce the possibility of complications in the fluorescence, arising from step-wise excitation of Hg atoms to high energy levels, and to avoid scattering in the spectrograph and spreading on the photographic plates of the otherwise very intense Hg lines 4358, 4047, and 3650–63, a filter was used. The filter cells were clamped in place and sealed with gaskets of soft

wax. The filter first used was a slightly acid solution of *p*-nitrosodimethylanaline[9] and nitrosodiethylanaline. When fresh the solution is quite efficient, but it deteriorates rapidly under strong illumination. Although a flowing supply can be used, the brown deposit which collects on the windows of the cell in the course of a few hours is bothersome. The filter finally adopted was a solution of $1M$ $NiSO_4$ and $1M$ $CoSO_4$,[10] which could be used for many hours without any apparent change in its transmission. An 8-mm layer transmits only a few percent in the region 5500A–3500A and approximately 60 percent at 2537A.

The fluorescence tube was used in a horizontal position, between two quartz mercury arcs. Self-absorption of the resonance line within the arcs was minimized by the usual devices—low current, water cooling, and a magnetic field. A quartz-fluorite achromat was used to project an image of the diaphragm at the exit window of the fluorescence tube onto the slit of the spectrograph.

The spectrograph employed for the spectrophotometry was a Hilger E–420, which is a quartz instrument designed for Raman effect work; it has a dispersion of 110 A/mm at 3900A. A few spectra were taken with a glass instrument with a dispersion of 9 A/mm at 3900A. Microphotometer traces were made with a Moll-type instrument.

V. Procedure

The measurements of intensity distribution were confined to the 4017 band, which arises from the transition $^2\Pi_i(v=0)\rightarrow{}^2\Sigma(v=0)$. It is the most intense band in the spectrum, and is not overlapped by any other bands of appreciable intensity. The bands toward greater wave-lengths are associated with the same upper state and so could not provide any additional information; those toward smaller wave-lengths are either weak or overlap badly.

Except under the most favorable conditions, the fluorescence was not sufficiently intense to permit the use of a spectrograph of high dispersion; consequently intensities of individual lines could not be measured. The procedure followed was to treat the band as a continuous spectrum and measure its profile under the various conditions of excitation. To test for the existence of a Boltzmann distribution among the rotational levels, and to estimate the rotational temperature, the profiles were compared with theoretical curves constructed in such a way as to show, for several values of rotational temperature, what the profile should be as observed under the actual conditions of resolving power.

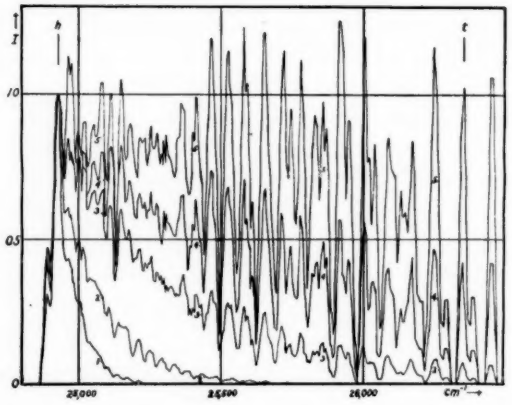

Fig. 2. Theoretical intensity distributions in the HgII 4017 band for various rotational temperatures.

Curve 1	Rot. Temp. = 296°K	$t/h = 10^{-11}$
2	936	10^{-5}
3	2960	0.07
4	9360	0.42
5	∞	1.02

The theoretical curves are shown in Fig. 2. Their construction was based on the approximation that the observed profile of a monochromatic line is a trapezoid 40 cm^{-1} wide at the base and 10 cm^{-1} wide at the top. Totals over all such trapezoids were taken at points 5 cm^{-1} apart.* Intensities of lines were computed from the formula:

$$I = i(j', j'')e^{-E(j')/kT}.$$

Term values of the *excited* state were used in the Boltzmann factor. The intensity factors i are those computed by Kapuscinski and Eymers[11] from the formulas derived by Hill and Van Vleck.[12] Term values and wave numbers were

[9] J. F. H. Custers and C. J. Dippel, Zeits. f. Physik **86**, 516 (1933).

[10] H. L. J. Bäckstrom, Naturwiss. **21**, 251 (1933).

* The actual method of computation was to add the intensities of all lines in each 5 cm^{-1} interval to obtain the sums I_1, I_2, ···. The summations $I_3' = I_1 + I_2 + \cdots + I_5$, etc. and $I_4'' = I_3' + I_4' + I_5'$, etc. were performed. I'' was taken as the resultant intensity at the middle of the 4th interval. Since $I_4'' = I_1 + 2I_2 + 3(I_3 + I_4 + I_5) + 2I_6 + I_7$, the lines have been distributed over trapezoids.

[11] W. Kapuscinski and J. G. Eymers, Zeits. f. Physik 54, 246 (1929).

[12] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

taken from the analysis by Hulthén.[13] The curve labeled $T=\infty$ was obtained by omitting the exponential factor in the above formula, and corresponds to the condition of completely chaotic excitation.

It should be noted that all of the curves indicate spaces of zero intensity between the lines in the tail of the band, consequently it is possible to judge the intensity of the background for that part of the band. Since the intensity rises abruptly at the head, the background can be estimated at that point also.

Calibration spectra for photometry were put on each plate by the method of calibrated wire gauzes.[14] The exposure time for the calibration spectra was two minutes; for the HgH spectra it varied from two minutes to two hours, depending on the contents of the fluorescence tube and the intensity of the primary radiation. Experiments were performed to determine how the intensity-contrast of the plates varied with exposure time. With M.Q. developer a correction for exposure time was necessary. During the course of the work attention was called to the fact that for certain varieties of Ilford plates developed with Rodinal the contrast had been found to be practically independent of exposure time.[15] Subsequent trials showed that within the limits $\frac{1}{2}$ minute–2 hours the variation in contrast was negligible for Cramer Hispeed plates developed with Rodinal. Spectra taken with a black-body furnace operated at a known temperature as the light source showed that the combined error arising from the variations in the dispersion of the spectrograph and the sensitivity of the plate was inappreciable for the wave-length range 4000A to 3700A.

The water used in the fluorescence experiments was purified by distillation from $KMnO_4$ and $Ba(OH)_2$ and several subsequent vacuum distillations. The possibility remained that during the course of an exposure the water vapor might become contaminated by its own decomposition products, for it is known that hydrogen is produced when water vapor is subjected to the action of excited Hg atoms.[16] Consequently the apparatus was arranged to supply the fluorescence tube with a continuous flow of water vapor. The pressure was varied by changing the exit capillary and the temperature at which the water was evaporated. At 17 mm pressure the rate of flow was about 1 cc/sec.; at 0.5 mm, 6 cc/sec.

Pure hydrogen was obtained by use of a palladium tube. One supply of nitrogen was produced by thermal decomposition of NaN_3, a second was high grade tank nitrogen further purified by means of a train consisting of a soda-lime column, a liquid-air trap, a tube of red hot copper shavings, and a second liquid-air trap.

It was not convenient to use flowing supplies of the permanent gases; contamination was prevented as far as possible by using a mercury seal to isolate the fluorescence tube from all stopcocks after the gases had been put in. In the case of two N_2–H_2O mixtures, tests for the effects of H_2 produced by decomposition of the water vapor were made by taking additional exposures with traces of hydrogen added beforehand.

VI. Experimental Results

Typical intensity distributions in the region 24,400 to 27,000 cm^{-1} (4100–3700A) of the sensitized-fluorescence spectra are shown in Figs. 3 and 4. Since the tail of the band is made up exclusively of high rotation lines and the head almost completely of low rotation lines, the ratio (intensity of tail/intensity of head), henceforth indicated by t/h, is a sufficiently good index of the abnormality of the rotational distribution. The intensity t is measured at 26,355 cm^{-1} and represents the combined intensity of the $R_1(27\frac{1}{2})$ and $Q_1(30\frac{1}{2})$ lines; h is measured at 24,930 and represents the sum of many overlapping lines, all with J values less than 14. The correlation between t/h and the rotational temperature, for cases in which a Boltzmann distribution exists, is shown in Fig. 2. (In estimating values of t/h from observed intensity distributions, the continuous background must be taken into account.)

H_2+N_2 (case A)

Experiments were performed with pressures of nitrogen varying from 0.9 to 160 mm. Spectra could not be obtained with pressures less than 0.9 mm because of the practically complete disappearance of HgH bands from the fluorescence.

[13] E. Hulthén, Zeits. f. Physik **32**, 32 (1925).
[14] G. R. Harrison, J. Opt. Soc. Am. **19**, 267 (1929).
[15] Ornstein, Moll and Burger, *Objective Spektralphotometrie* (1932), p. 51.
[16] H. Senftleben and I. Rehren, Zeits. f. Physik **37**, 529 (1926).

(No attempt was made to find any relation between the intensity distribution and the pressure of hydrogen, which was never greater than 0.02 mm; any considerable addition of hydrogen in the sensitized-fluorescence experiments quenches all fluorescence radiation entirely.) Some of the intensity distributions obtained are reproduced in Fig. 3. The values of t/h for the entire series of measurements are plotted against the pressure of nitrogen in Fig. 5.

Over the entire range of pressures, the results indicate that the distribution of excited molecules among the rotational levels diverges radically from the distribution consistent with the temperature of the gas. Although the fluorescence tube was at room temperature throughout the experiments, the lowest value of t/h (0.32, for 0.9 mm N_2) corresponds to a rotational temperature of nearly 10,000°. The occurrence of a value of t/h as great as 4.4 (for 80 mm N_2) is remarkable, inasmuch as the Boltzmann formula for the distribution among rotational levels could be made consistent with a value of t/h greater than 1.0 only if a negative (absolute) temperature were introduced in the formula; obviously in this case a rotational temperature has no physical significance whatever.

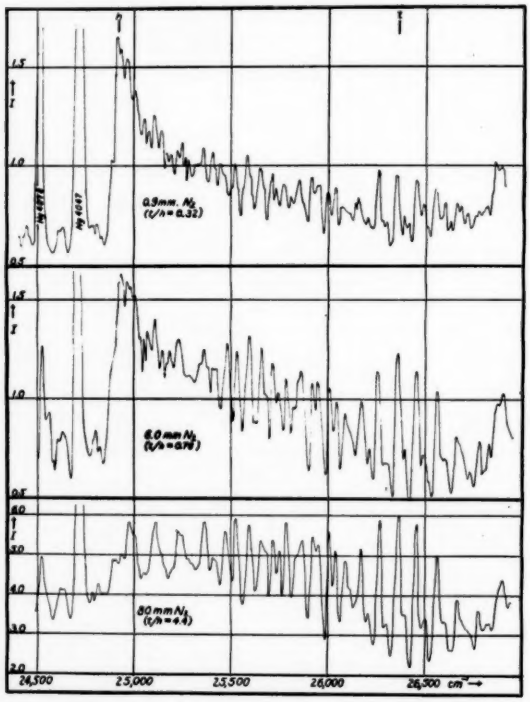

FIG. 3. Observed intensity distributions in the HgH 4017 band, case A (N_2+trace of H_2). The scale of ordinates in each case has been chosen to make the intensity of the band head approximately one unit above the background.

The intensity distributions show a pronounced dependence on the pressure of nitrogen; t/h increases continuously from 0.32 to 4.4 as the pressure is raised from 0.9 to 80 mm; but decreases slightly when the pressure is further increased from 80 to 160 mm.

H_2O (case B)

Experiments were performed with pressures of water vapor ranging from 0.7 mm to 17 mm; the observed values of t/h are plotted against the pressure of water vapor in Fig. 5. The intensity curves for pressures 0.7 mm, 1.5 mm and 3.2 mm are reproduced in Fig. 4. The present results fail to confirm the observation made by Beutler and Rabinowitch[2] that the intensity distribution for case B corresponds to room temperature,* and that it is independent of the pressure of water vapor.

That the distribution among rotational levels of the excited state is not consistent with the temperature of the gas is shown by the values of t/h; the observed values are all greater than 0.05, which is to be compared to the value of 10^{-11} predicted for a rotational temperature of 296°K. The dependence of the intensity distribution on the pressure of water vapor is demonstrated by the way both t/h and the details of the intensity curves change with the pressure; the high rotation lines are relatively more intense at the lowest pressure. Although it would have been desirable to extend the measurements to a wider range of pressures, experimental difficulties prevented it. With less than 0.7 mm of water vapor the HgH bands were so weak, compared with the Hg lines and continuous background, that no measurable spectra could be obtained.

* Exception to this observation may also be taken on the basis of Figs. 1 and 2 of Beutler and Rabinowitch's paper (reference 2, pp. 411, 418). Their reproduction of the spectrum (Fig. 1b) shows two lines of the 4219 band ($v'=0$, $v''=1$) which fall between the Hg 4047 line and the head of the 4017 band; both apparently have intensities comparable with the other lines of the same band. One of these lines is the $Q_1 22\frac{1}{2}$ line, the other is made up of the overlapping $R_1 20\frac{1}{2}$ and $QR_{12} 21\frac{1}{2}$ lines (Hulthén's notation —$Q_2(23)$, $R_2(21)$, and $R_1(22)$). Curve a of their Fig. 2 shows that at room temperature states with rotational quantum number greater than 15 have vanishingly small populations; the observed intensity distribution is therefore far from normal.

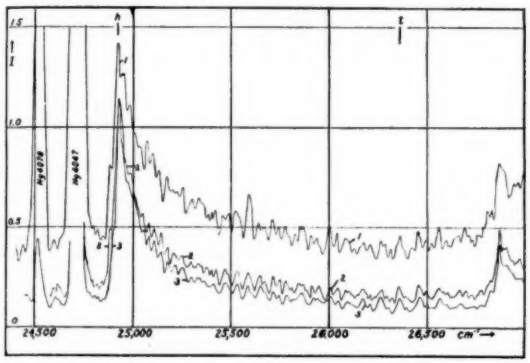

FIG. 4. Observed intensity distributions in the HgH 4017 band, case B (H_2O).

Curve 1	0.7 mm H_2O	$t/h=0.12$
2	1.5	0.07
3	3.2	0.07

Extension of the measurements to pressures higher than 20 mm (vapor pressure of water at room temperature) would have necessitated complete reconstruction of the apparatus.

The nonoccurrence of a Boltzmann distribution among rotational levels of the excited state is evidenced by the inconsistencies between the theoretical and observed intensity curves. For instance, when the curve obtained with 3.2 mm of water vapor is compared with the curves in Fig. 2 it is found that the profile of the band head (24,350 to 27,000 cm^{-1}) is quite similar to the theoretical curve for $T=296°$, but that the intensity of the extreme tail of the band accords better with a temperature of about 3000°. A similar, but less pronounced departure from a Boltzmann distribution for HgH bands, excited in an electric discharge through hydrogen and mercury vapor, has been observed by Kapuscinski and Eymers.[11]

H_2O+N_2 (case C)

The values of t/h observed for mixtures of water vapor and nitrogen, and in two cases with similar mixtures containing traces of hydrogen, are given in Table I. It is apparent that the addition of traces of hydrogen causes no change in the value of t/h observed; the intensity curves (not shown) demonstrate even more conclusively that the hydrogen does not influence the intensity *distribution*. Nevertheless the hydrogen did change the total intensity of the bands, reducing it decidedly in both cases; it thus

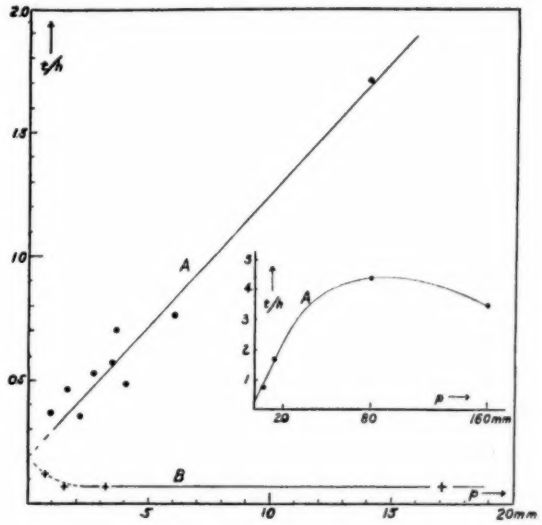

FIG. 5. Observed values of t/h plotted against pressure of N_2 for case A (dots) and against the pressure of water vapor for case B (crosses). The inset shows the values for the higher pressures of N_2.

seems reasonable to assume that the amount of hydrogen added was sufficient to play a significant part in the reactions connected with the fluorescence. The remaining results may be summarized in the following generalizations:

(1) For any mixture of p mm N_2 and r mm H_2O, the observed value of t/h is lower than would have been obtained with p mm N_2 and a trace of H_2, but greater than with r mm H_2O only.

(2) For a fixed pressure of H_2O, t/h increases as the pressure of N_2 is raised.

(3) For a fixed pressure of N_2, t/h decreases as the pressure of H_2O is raised.

INTERPRETATION OF RESULTS

The occurrence of the HgH bands in the sensitized fluorescence experiments is adequately explained by the elementary processes assumed

TABLE I. *Observed values of t/h for case C (H_2O+N_2).*

p, H_2O (mm)	p, N_2 (mm)	p, H_2 (mm)	t/h
0.4	2.7	—	0.23
0.4	2.6	0.01	0.23
0.16	3.6	—	0.38
0.17	3.5	0.005	0.42
1.0	3.6	—	0.22
1.0	10	—	0.48
1.0	67	—	2.3

by Beutler and Rabinowitch—formation of an unexcited HgH molecule in an exchange reaction and subsequent electronic excitation of the molecule by a collision of the second kind, with a metastable mercury atom taking part in each process. For the arguments in support of these processes, the reader may consult the original paper.[2] The above explanation of the *occurrence* of the bands appears to be entirely consistent with the results of the present experiments, and provides the starting point for their interpretation.

However, the following three objections may be raised against Beutler and Rabinowitch's attempt to interpret the difference in *intensity distributions* for cases A and B entirely on the basis of the energy relations in the formation processes (1a) and (1b). These objections are based on the more exact knowledge of the intensity distributions for cases A and B which has been obtained by the use of photographic photometry, and on the new experiments with both H_2O and N_2 in the fluorescence tube.*

(1) The assumption that the entire excess rotation observed in the emission spectrum arises from the formation process necessitates the additional assumption that the molecule in its *normal* state must retain the rotational energy for an appreciable period of time (perhaps 10^{-4} or 10^{-3} second), until an excited Hg atom is encountered. This hypothesis encounters the difficulty that when the HgH molecule is in its normal electronic state and in a very high rotational level, it exhibits the phenomenon of dissociation-by-rotation; a molecule formed with very great rotational energy would dissociate before the excitation process 3 could occur. Nevertheless, lines of the 4017 band up to $J'=32\frac{1}{2}$ occur in sensitized fluorescence, although for the normal electronic state, the rotational energy exceeds the energy of dissociation for all values of J greater than $24\frac{1}{2}$. The spectra with a dispersion of 9 A/mm show the $J'=32\frac{1}{2}$ lines broadened as a consequence of the extremely small lifetime of corresponding rotational levels of the normal, $^2\Sigma$, state*; to explain the occurrence of these lines, one must assume that the molecule acquires at least part of its rotation during the lifetime of the excited state, which has a much higher dissociation energy than the normal electronic level.

(2) As shown in Section III, the assumption that the formation process alone determines the intensity distribution leads to the prediction that the distribution for case C (H_2O+N_2) should resemble that for case B (H_2O) rather than case A (H_2+N_2). This prediction is disproved by the experimental results, for although the maximum observed value of t/h for case A is 0.12, the values for case C range from 0.22 to 2.3 and are thus comparable to the values for case A, which run from 0.32 to 4.4.

(3) Beutler and Rabinowitch justified their assumption that collisions during the lifetime of the excited state do not change the rotation of the HgH molecule principally by their failure to detect any dependence of the intensity distribution for B on the pressure of water vapor. Apparently they made no investigation of the effect of varying the pressure of N_2 in case A. The present experiments give some indication that for case B there is actually a slight difference in the intensity distributions for 0.7 mm and for 1.5 mm H_2O. They demonstrate conclusively that the pressures of H_2O and N_2 both influence strongly the intensity distribution for case C, and that the pressure of N_2 has a pronounced influence on the intensity distribution for case A. An increase in the pressure of N_2 for either case A or C results in an increase in the average rotational energy of the HgH $^2\Pi_{\frac{1}{2}}(v=0)$ molecules, and there appears to be no possibility of explaining this behavior in terms of the formation process, which does not involve the N_2 molecule at all.

In view of the foregoing arguments, it is evident that the characteristics of the intensity distributions cannot be explained merely on the basis of the energy relations for the chemical process in which the unexcited HgH molecule is formed.

The alternative interpretation of the difference between the intensity distributions for cases A and B, suggested by Oldenberg, has been reviewed in Section II of this paper. If, as Oldenberg has proposed, collisions with N_2 molecules which occur during the lifetime of the excited HgH molecule can increase the rotational energy of the latter at the expense of its vibration, the probability of such processes should increase with the pressure of N_2, and the proportion of excited molecules in high rotational levels should accordingly increase with the pressure of N_2. The observed intensity distributions show

* Apart from the question of what influence the formation process may actually have on the emission spectrum observed in the sensitized fluorescence experiments, there may be some doubt as to whether an endothermic reaction necessarily leads to the formation of molecules with only the thermal value of rotational energy. Whenever the energy of activation is considerably greater than the energy of reaction, there is present a factor which restricts the occurrence of the chemical process to just those collisions in which the thermal energy happens to be great enough to supply the energy of activation. Upon the completion of the process, the excess of the energy of activation above the energy of reaction must be distributed among the various degrees of freedom of the reaction products, and there is no *a priori* reason to suppose that none of this energy may go into rotation.

* The half-value width of the $J'=32\frac{1}{2}$ lines is approximately 4 cm^{-1}, which corresponds to a mean lifetime of the order of magnitude of 10^{-11} sec.

just this behavior for both cases A and C, and the effect is very pronounced. The main idea of Oldenberg's explanation of the difference between the rotational distributions for cases A and B thus finds confirmation in the new experiments. Nevertheless his theory, based on a classical treatment of collision processes, oversimplifies the phenomena, as will become evident from the following more detailed discussion.

In order to understand the detailed behavior of the intensity distributions it is necessary to examine the following sequences of processes:

Case A	Case B
$Hg'+H_2 \rightarrow HgH+H$	$Hg'+H_2O \rightarrow HgH$
$+0.62$ v (1a)	-0.1 v (1b)
$\sim 10^4$ collisions	$\sim 10^4$ collisions
$HgH+N_2$ (2a)	$HgH+H_2O$ (2b)
$Hg'+HgH \rightarrow Hg+HgH'$ (3)	$Hg'+HgH \rightarrow Hg+HgH'$ (3)
a few collisions	a few collisions
$HgH'+N_2$ (4a)	$HgH'+H_2O$ (4b)
$HgH' \rightarrow HgH+h\nu$ (5)	$HgH' \rightarrow HgH+h\nu$ (5)

(Hg′ denotes Hg 6^3P_0)

Case C involves no new processes, the sequence is (1a), (2a) and (2b), (3), (4a) and (4b), (5). The correct interpretation of the experimental results should lead to consistent answers to the questions: In which processes do HgH molecules receive rotational energy in excess of the thermal value? and: In which processes are HgH molecules deprived of excess rotational energy? (In what follows, the elementary processes are referred to according to the numbering given above, rather than by that used in Section II.)

Collisions between N_2 and excited HgH molecules (4a)

For case A, any increase in the pressure of N_2, in the range 1 to 80 mm, enhances the abnormal rotation of HgH molecules in the $^2\Pi_{\frac{1}{2}}(v=0)$ state; at the higher pressures, molecules with rotational energy greater than 0.4 v predominate. This effect cannot be attributed to changes in the formation process (1a) or the excitation process (3), for it is to be expected that Hg 6^3P_0 atoms predominate in these processes because of their overwhelming concentration compared to Hg atoms in other excited states. The phenomenon must be interpreted as a consequence of collisions 4a between excited HgH and normal N_2 molecules: process 3 results in the excitation of HgH molecules to higher vibrational or electronic levels, as well as to the $^2\Pi_{\frac{1}{2}}(v=0)$ state, and subsequent collisions with N_2 transfer the highly excited molecules to the upper rotational levels of the $^2\Pi_{\frac{1}{2}}(v=0)$ state. The process is essentially a redistribution of excitation energy among the degrees of freedom of the HgH molecule. Apparently, when the pressure of nitrogen is as great as 80 mm, this process almost completely quenches the highly excited states which are involved, for t/h fails to increase further when the pressure of N_2 is increased from 80 to 160 mm. The identity of the highly excited states of HgH which take part in this process will be discussed later, in connection with the excitation process.

One should expect that at some very high pressure collisions with N_2 must become effective in reducing the abnormal rotation of the HgH $^2\Pi_{\frac{1}{2}}(v=0)$ molecules toward the thermal value, resulting in decreased values of t/h, unless it should happen that the probability of quenching the excited HgH molecule to the normal electronic state is greater than the probability for the transfer of rotational energy in a collision. However, the total intensity of the 4017 band (judged by the exposure time necessary for obtaining spectra) is not strongly influenced by the pressure of N_2 in the range 3 to 160 mm; evidently the $^2\Pi_{\frac{1}{2}}(v=0)$ state is quite stable against quenching by N_2. The observed value of t/h for 160 mm N_2 is only slightly less than that for 80 mm; thus we may conclude that there is only a small probability for an exchange of rotational energy in a collision between a normal N_2 molecule and a HgH molecule in the lowest excited state.

The above conclusions are consistent with the observations for case C, which show that, with a fixed pressure of water vapor, the average rotational energy of the HgH $^2\Pi_{\frac{1}{2}}(v=0)$ molecules increases with the higher pressures of N_2.

Collisions between H_2O and excited HgH molecules (4b)

For case B, the average rotational energy of HgH molecules in the $^2\pi_{\frac{1}{2}}(v=0)$ state decreases as the pressure of water vapor is raised from 0.7 to 1.5 mm, but no subsequent change is noticeable when the pressure is further increased to as

much as 17 mm. At the higher pressures the distribution of molecules among the rotational levels attains a limiting form which does not correspond at all to the temperature of the gas inasmuch as it contains far too large a proportion of molecules with rotational energy greater than 0.2 v. The variation in intensity distribution is evidently the result of collisions between excited HgH and normal H_2O molecules. But the simplest interpretation—that in collisions the excess rotational energy of the HgH is partly taken up by the H_2O molecules as suggested by Oldenberg—cannot be correct; if it were, then the proportion of molecules in the higher rotational levels would continue to fall toward the thermal value when the pressure is increased above 1.5 mm. One must in fact conclude from the observed constancy of the intensity distribution over the range 1.5 to 17 mm that collisions with H_2O are rather ineffective in changing the rotational energy of a HgH molecule in the $^2\Pi_{\frac{1}{2}}(v=0)$ state. The true explanation of the variation in intensity distribution appears to be that collisions with H_2O lower the average rotational energy by transferring molecules from highly excited states to the *low* rotational levels of the $^2\Pi_{\frac{1}{2}}(v=0)$ state; that is, part of the excitation energy of the HgH is taken up by the H_2O molecule, instead of being redistributed among the degrees of freedom of the HgH as in the case of collisions with N_2.

Presumably the intensity distribution is altered by only the first few mm of water vapor because the collisions are very effective for the above process—1.5 mm of water vapor is sufficient to quench almost completely the upper states of HgH which are involved. The great effectiveness of H_2O for the process just discussed is also demonstrated by the observations for case C; with the pressure of N_2 fixed at 3.5 mm, increasing the pressure of water vapor from 0.16 to 1.0 mm results in a decrease in t/h from 0.40 to 0.22. In this case we are dealing with a competition of processes; both H_2O and N_2 transfer molecules from some highly excited state to the $^2\Pi_{\frac{1}{2}}(v=0)$ state, the former to the low rotational levels, the latter to high ones.

Formation processes ((2a) and (2b))

Although the formation processes can in no case be the source of the entire abnormal rotation observed, the question remains as to what contribution, if any, these processes actually do make to the rotational energy indicated by the *emission* spectrum of the HgH molecule. It is obvious that under ordinary conditions the processes previously discussed mask whatever contribution the formation processes may make to the abnormal rotation observed in the emission spectrum. However, the influence of this one type of process—collisions during the lifetime of the *excited* molecule—must become relatively unimportant as the pressure of the foreign gas is reduced indefinitely.

Although the experiments cannot be carried out when the pressure is reduced below certain limits, the intensity distribution characteristic of zero pressure of the foreign gas may be estimated by extrapolating to zero pressure from the actual measurements obtained at low pressures. The extrapolation may be made on the basis of the data collected in Fig. 5. Since, in the presence of 1 mm of water vapor or nitrogen, the HgH molecule suffers only about 6×10^6 collisions per second (assuming a collision radius of 3×10^{-8} cm), the extrapolation to zero pressure from the range 0.7 to 3.0 mm has the significance of correcting for the effect of collisions during the lifetime of the excited state. The value of t/h for zero pressure of nitrogen is estimated to be 0.25 ± 0.05; for zero pressure of water vapor, 0.20 ± 0.05; the corresponding values of rotational temperature are $7000°\pm1000°$ and $6000°\pm1000°$, respectively. The distribution among rotational levels corresponding to these values of t/h must be the result of the first three steps only in the respective sequences of elementary processes. As sources of abnormal rotation only the formation processes (1a) and (1b) and the excitation process (3) need be considered. In the two formation processes, the chemical energy available for rotation is very different: 0.62 v in (1a), none at all in (1b). It seems very unlikely that among molecules formed in the respective reactions, a high, equal proportion should occur with rotational energy greatly in excess of the thermal value. Nevertheless there is no indication of a great dissimilarity in the intensity distributions for cases A and B under conditions such that collisions during the lifetime of the excited state may be neglected entirely. On the contrary,

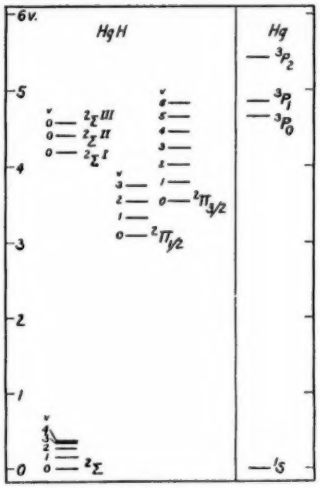

FIG. 6. Electronic and vibrational levels of the HgH molecule, and the lower energy levels of the Hg atom.

there is fairly good evidence that the distributions are similar, and consequently it is more plausible that under such conditions the abnormal rotation has its source principally in the process which is common to both sequences—the excitation process 3, and that the contribution of either formation process to the abnormal rotation exhibited by the emission spectrum is comparatively small.

It is not contended that neither of the reactions (1a) or (1b) leads to molecules with any excess rotational energy, but rather that whatever rotation originates in either of the formation processes and survives the collisions (2a) or (2b) is negligible compared with that arising from the excitation process. Accordingly, the formation process may be left entirely out of account in any attempt to interpret the relation between the intensity distribution and the pressure of a foreign gas.

The excitation process (3): Energy levels of HgH excited in collision of the second kind with Hg 6^3P_0 atoms

In sensitized fluorescence, HgH molecules can receive excitation energy only through collisions of the second kind with excited Hg atoms. Under the conditions of the experiments—nearly a mm of H_2O or N_2 must be present if the HgH spectrum is to be observed—the concentration of Hg 6^3P_0 atoms very greatly exceeds that of atoms in other excited states. The excitation process (3) thus may be considered to be a constant factor under all conditions; but the distribution of HgH molecules among the various energy levels which results from this process is modified by collisions with foreign molecules necessarily present. The distribution among rotational levels of the $^2\Pi_{\frac{1}{2}}(v=0)$ state which is approached as the pressure of N_2 or H_2O is reduced toward zero is very probably characteristic of the excitation process only, as has been shown in the preceding paragraphs, and we may conclude that at least among molecules excited to this state, there are an appreciable proportion in the high rotational levels.

In order to explain the way in which the intensity distribution in the 4017 band is influenced by the various foreign gases it has been necessary to assume that some HgH molecules are excited to states of greater energy than about 4 v, and that the foreign gases transfer molecules from these states to either high or low rotational levels of the $^2\Pi_{\frac{1}{2}}(v=0)$ state. Hulthén's[17] and Rydberg's[18] analyses of the spectrum excited by the electric discharge show that HgH has three $^2\Sigma$ states and also vibrational levels of the $^2\Pi_{3/2}$ state which have excitation energies between 4 and 5 v; the energy level diagram of HgH is reproduced in Fig. 6. One would expect to find bands associated with one or more of the highly excited states in the sensitized fluorescence spectra obtained with very little foreign gas present; these bands should disappear when the pressure is increased.

The spectra obtained with nitrogen lend some support to the above ideas. With 1.6 mm of N_2, several bands in the ultraviolet appear, but spectra taken with higher pressures of N_2 fail to show any bands of wave-length shorter than 2900A even when the 4017 band is equally exposed. No intensity measurements were made on the ultraviolet bands, but the phenomenon is clearly demonstrated by the microphotometer traces in Fig. 7. The upper trace is from a spectrum taken with 1.6 mm of N_2 in the fluorescence tube; the lower, with 14 mm of N_2. Bands at 2878 and 2823, which arise from the 4th and 5th vibration levels of the $^2\Pi_{3/2}$ states, appear clearly in the former but are extremely

[17] E. Hulthén, Zeits. f. Physik **50**, 319 (1928).
[18] R. Rydberg, Zeits. f. Physik **73**, 74 (1931).

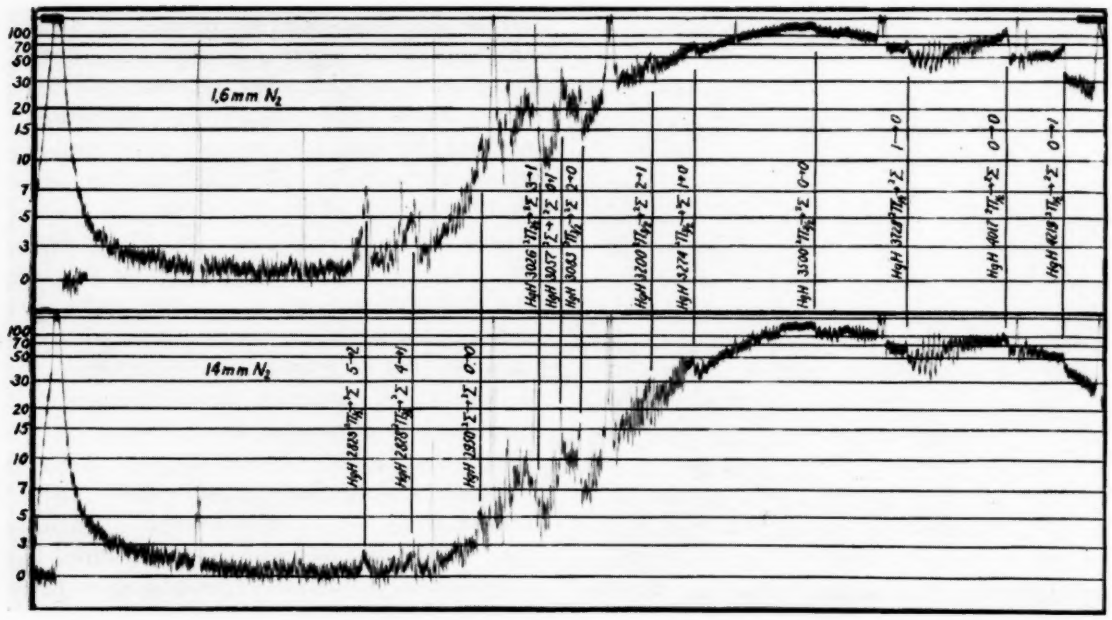

FIG. 7. Microphotometer traces of HgH spectra excited by sensitized fluorescence, case A. Upper curve, 1.6 mm N_2; lower curve, 14 mm N_2. The intensity scales at left correspond to the plate calibration at 3800A.

weak in the latter, so there is some evidence that it is partly vibrational and partly electronic energy which is transferred into rotation by collisions with N_2. Only the heads of the 2878 and 2823 bands appear, as is to be expected if excitation is by collisions with 6^3P_0 Hg atoms, since in that case less than 0.2 v energy is available for rotation.

In addition to the bands which have been discussed, nearly all of the remaining known HgH bands which have excitation energies lower than that of the Hg 6^3P_0 atom can be identified in long exposure spectra for case A. (Many of the bands cannot be observed for cases B and C because the region 3300–2537A is obscured by an intense continuous spectrum whenever water vapor is present in the fluorescence tube.) Since the relative intensity of some of the bands is influenced by collisions, the exact distribution among vibrational and electronic levels which is characteristic of the excitation process alone could be obtained only from an intensity distribution for the entire spectrum extrapolated to zero pressure of the foreign gas. The data necessary for such an extrapolation would be very difficult to secure because many of the bands overlap, but some idea of the distribution characteristic of the excitation process may be obtained from spectra for very low pressures of N_2, for example that illustrated by the upper trace in Fig. 7. It is remarkable that the bands in the region 3000 to 2800 are relatively weak even though these are the bands which have excitation energies very nearly equal to that of the Hg 6^3P_0 atom. Even when some allowance is made for the partial quenching of some of these bands by the small amount of N_2 present, and for a falling off by a factor of possibly five in the sensitivity of the photographic plate at 2800A compared to the sensitivity at 4000A, there is no indication that the probability for excitation of the various electronic and vibrational states of HgH is related to the closeness of resonance with the Hg 6^3P_0 atom.

Beutler and Rabinowitch,[2] who were the first to point out the above peculiarity in the intensity distribution, suggested that the high rate of excitation of the $^2\Pi_{\frac{1}{2}}(v=0)$ state might be the consequence of a secondary process: Molecules are first excited to some state having close resonance with the Hg 6^3P_0 atom, and then fall to the $^2\Pi_{\frac{1}{2}}(v=0)$ state with the emission of infrared radiation. The energy difference 4.65 v -3.05 v corresponds to a band in the region

8000 to 9000A. Attempts to find such bands in the sensitized fluorescence spectra, by Beutler and Rabinowitch, and by the author (using the new infrared sensitive plates of the Eastman Kodak Company) have been unsuccessful. Beutler and Rabinowitch reported finding infrared bands in a water-cooled mercury arc containing hydrogen; but the present author has been unable to find such bands in a mercury vapor-hydrogen discharge even though the exposure times were many thousands of times greater than that required to photograph the 4017 HgH band. There appears to be no report in the literature of any infrared HgH bands, although there is no reason why they should not exist. Transitions from the excited $^2\Sigma$ states to the $^2\Pi_{\frac{1}{2}}(v=0)$ state would lead to bands with origins at 11,200, 9400, and 8300A, and one corresponding transition is known in the spectrum of the closely related CdH molecule.[19] However, in the absence of any experimental confirmation, the assumption, merely on the basis of the resonance condition, that the emission of an infrared band must play a part in the excitation of the $^2\Pi_{\frac{1}{2}}(v=0)$ state in sensitized fluorescence is hardly justified, for there are additional examples which seem to indicate that close resonance is not always necessary for the excitation of molecules in collisions of the second kind. The OH bands can be excited by Hg-sensitized fluorescence,[1] and the 3064 band is always much stronger than the 2811 band even though the excitation energies are, respectively, 4.0 v and 4.4 v. It is interesting to note that these bands also exhibit abnormal rotation. The observation by Olsen[20] that the violet CN bands sometimes occur in Hg-sensitized fluorescence, presumably because of contamination by stopcock grease, has been confirmed often in the course of these experiments; in addition the infrared CN bands were observed in the course of the search for infrared HgH bands in sensitized fluorescence. The excitation energies of the two sets of CN bands are approximately 3 v and 2 v, respectively. NH bands, with an excitation energy of 3.7 v, can also be excited by Hg-sensitized fluorescence.[1]

[19] Svensson, Zeits. f. Physik **59**, 333 (1930).
[20] O. Olsen, Phys. Rev. **48**, 476(A) (1935).

VIII. Conclusions

It has been shown that the abnormal rotation indicated by the intensity distribution in the spectrum of HgH excited by sensitized fluorescence is the result of elementary processes which occur during the lifetime of the *excited* state of the molecule. There are two types of process in which the molecule receives rotational energy in excess of the thermal value:

(1) Collisions of the second kind with metastable Hg atoms in which the excitation energy of the atom is taken up partly as rotational and partly as electronic energy of the molecule, and

(2) Collisions of the second kind between highly excited HgH molecules and normal N_2 molecules, in which excitation energy is redistributed among the degrees of freedom of the HgH molecule—vibrational and electronic energy is transferred into rotation.

Collisions with H_2O molecules are found to be very effective in transferring HgH molecules from a highly excited state—very probably $^2\Pi_{3/2}(v=4)$—to the lowest excited state; the difference in energy of the two states is mostly taken up by the H_2O, rather than the HgH molecule.

The chemical process in which the HgH molecule is formed has been found to have practically no influence on the intensity distribution in the emission spectrum. Consequently the argument on which Beutler and Rabinowitch based their conclusion that abnormal rotation of the normal HgH molecule could withstand many thousands of collisions with N_2 molecules is not valid. However, some entirely new evidence which indicates a considerable persistence of rotation in collisions between normal HgH and N_2 molecules will be published in a subsequent paper.

Additional experiments have been made to find the influence of collisions with helium and argon atoms on the rotation of the HgH molecule. A report of these experiments and a comparison between the effective cross sections of N_2, H_2O, He, and A for the various types of elementary process which occur will be given in a third paper of the series.

In conclusion, the author wishes to express his gratitude to Professor Oldenberg, who directed this work, for many helpful discussions concerning both the experimental technique and the interpretation of the results.

The Effect of Rotational Distortion on the Thermodynamic Properties of Water and Other Polyatomic Molecules

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The classical mechanical expression for the energy of a non-vibrating, rotating polyatomic molecule is obtained which includes a correction term arising from the centrifugal distortion of the molecule caused by the rotation. Since the rotational partition function closely approaches the classical phase integral for room temperatures or higher, the latter is used to calculate the effect of centrifugal distortion on the entropy, heat capacity and free energy. The correction terms $-\rho RT^2$, $2\rho RT$ and $2\rho RT$ must be added to F, S and C_v, respectively. ρ is a constant characteristic of each molecule. The values of ρ calculated are: H_2O, 2.04 10^{-5}; H_2S, 1.62 10^{-5}; NH_3, 1.45 10^{-5}; CH_4, 1.72 10^{-5}; C_2H_4, 0.79×10^{-5}. For water this correction amounts to approximately ½ percent of the heat capacity at the boiling point, or +0.032 entropy unit.

IT is customary in calculating the thermodynamic properties of polyatomic molecules from spectral data to assume that the partition function can be separated into three factors, corresponding to the separation of the energy into the translational, rotational, and vibrational parts. Furthermore, it has been found to be a good approximation to use the classical limiting values for the translational and rotational factors for room temperature or above. Ordinarily, the rotational partition function is computed for a rigid rotator, neglecting any effect due to the distortion caused by rotation. It is the purpose of this paper to show how this distortional effect can be included in the calculations and to point out that it is not a negligible correction for certain light molecules with weak bending restoring forces. Classical mechanics will be used throughout.

The Phase Integral for the Rigid Rotator

The classical limiting expression for the rotational partition function is the phase integral [1]

$$Q_R=(1/h^3)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi}e^{-W_R/kT}\times d\varphi d\theta d\chi dp_\varphi dp_\theta dp_\chi, \quad (1)$$

in which the Eulerian angles φ, θ and χ and their conjugate momenta p_φ, p_θ and p_χ have been used. h is Planck's constant, and W_R the rotational energy. For our purposes, it is more convenient to express W_R in terms of P_x, P_y and P_z, the components of the angular momentum along a set of Cartesian axes x, y and z moving with the molecule. The relations between P_x, P_y, P_z and p_φ, p_θ, p_χ are[2]

$$p_\theta=\sin\chi\,P_x+\cos\chi\,P_y,\quad p_\chi=P_z,$$
$$p_\varphi=-\sin\theta\cos\chi\,P_x+\sin\theta\sin\chi\,P_y+\cos\theta\,P_z. \quad (2)$$

The Jacobian of this transformation is $\sin\theta$. Consequently, the phase integral becomes

$$Q_R=(8\pi^2/h^3)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-W_R/kT}dP_xdP_ydP_z, \quad (3)$$

where the new set of variables φ, θ, χ, P_x, P_y, P_z has been introduced and the integration carried out over $d\varphi d\theta d\chi$, since in terms of the new variables W_R is independent of the angles.

The energy of a rigid rotator is given by

$$W_R{}^0=\tfrac{1}{2}(P_x{}^2/A_0+P_y{}^2/B_0+P_z{}^2/C_0), \quad (4)$$

in which A_0, B_0, C_0 are the principal moments of inertia. On inserting this in the integral for Q_R, the result is obtained that

$$Q_R{}^0=(8\pi^2/h^3)(2\pi kT)^{\frac{3}{2}}(A_0B_0C_0)^{\frac{1}{2}}, \quad (5)$$

which is the usual result. From it one obtains the well-known expressions for the contribution of the rotation to the free energy F, entropy S, and heat capacity C_v, by using the relations

$$F=-RT\log Q;\quad S=R\log Q+RT(d\log Q/dT) \quad (6)$$
$$C_v=2RT(d\log Q/dT)+RT^2(d^2\log Q/dT^2),$$

in which R is the gas constant.

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[1] See R. H. Fowler, *Statistical Mechanics*, p. 44.

[2] See for example, E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936), Eq. (30).

Calculation of the Rotational Distortion

For semi-rigid polyatomic molecules the classical energy of rotation and vibration is given by[3]

$$W=\tfrac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}(P_\alpha-p_\alpha)(P_\beta-p_\beta)+\tfrac{1}{2}\sum p_k^2+V, \quad (7)$$

in which α, $\beta=x,y$, or z, p_α is the α component of the vibrational angular momentum, P_α is the corresponding component of the total angular momentum, and p_k is the momentum conjugate to the normal coordinate Q_k. The coefficients $\mu_{\alpha\beta}$ are the elements of the matrix reciprocal to the matrix

$$\begin{pmatrix} A' & -D' & -F' \\ -D' & B' & -E' \\ -F' & -E' & C' \end{pmatrix},$$

in which A', B', C' are equal (up to quadratic terms in Q_k) to the instantaneous moments of inertia, while D', E', F' are similarly related to the instantaneous products of inertia. All these quantities are functions of the normal coordinates. V is the potential energy.

If we assume that the molecule is not vibrating, so that p_k and $\dot{p}_k$ are zero, then it is found that p_α and $\partial p_\alpha/\partial Q_k$ are zero. Consequently, one of Hamilton's equations can be written in the form

$$\frac{\partial H}{\partial Q_k}=\tfrac{1}{2}\sum_{\alpha,\beta}\frac{\partial \mu_{\alpha\beta}}{\partial Q_k}P_\alpha P_\beta+\frac{\partial V}{\partial Q_k}=-\dot{p}_k=0. \quad (8)$$

For harmonic forces (an approximation) the potential energy can be written

$$V=\tfrac{1}{2}\sum_k \lambda_k Q_k^2, \quad (\lambda_k=4\pi^2\nu_k^2), \quad (9)$$

with ν_k signifying the frequency of the normal vibration Q_k. Furthermore, the quantity $\mu_{\alpha\beta}$ can be expanded into the form

$$\mu_{\alpha\beta}=\mu_{\alpha\beta}^0+\sum_k \mu_{\alpha\beta}^{(k)}Q_k+\cdots, \quad (10)$$

in which $\mu_{\alpha\beta}^0$ is the equilibrium value and

$$\mu_{\alpha\beta}^{(k)}=(\partial\mu_{\alpha\beta}/\partial Q_k)_0. \quad (11)$$

[3] Ref. 2, Eq. (13).

Consequently, if higher powers of Q_k are neglected, Eq. (8) gives

$$Q_k=-(1/2\lambda_k)\sum_{\gamma,\delta}\mu_{\gamma\delta}^{(k)}P_\gamma P_\delta \quad (k=1, 2, \cdots, 3N-6), \quad (12)$$

so that

$$\mu_{\alpha\beta}=\mu_{\alpha\beta}^0-\tfrac{1}{2}\sum_{\gamma,\delta,k}\mu_{\alpha\beta}^{(k)}\mu_{\gamma\delta}^{(k)}P_\gamma P_\delta/\lambda_k. \quad (13)$$

These expressions for $\mu_{\alpha\beta}$, Q_k and V, when inserted into Eq. (7) yield

$$W_R=\tfrac{1}{2}\sum_{\alpha\beta}\mu_{\alpha\beta}^0P_\alpha P_\beta-(1/8)\sum_{\alpha,\beta,\gamma,\delta,k}\times(\mu_{\alpha\beta}^{(k)}\mu_{\gamma\delta}^{(k)}/\lambda_k)P_\alpha P_\beta P_\gamma P_\delta \quad (14)$$

for the rotational energy, including a correction for the rotational distortion. The coefficient $-1/8$ is made up of a contribution $-1/4$ from the kinetic energy and $+1/8$ from the increased potential energy.

It is not necessary to use normal coordinates to get the above results, and in actual applications other coordinates are frequently more convenient. In terms of the $3N-6$ internal coordinates q_i, the potential energy is

$$V=\tfrac{1}{2}\sum b_{ij}\,q_i\,q_j, \quad (15)$$

to the same approximation as before. The constants b_{ij} are the force constants. The coefficients $\mu_{\alpha\beta}$ can be expanded in terms of the q_i's, with the result that

$$\mu_{\alpha\beta}=\mu_{\alpha\beta}^0+\sum\bar{\mu}_{\alpha\beta}^{(i)}q_i+\cdots. \quad (16)$$

Consequently the analogue of Eq. (12) is

$$\tfrac{1}{2}\sum\bar{\mu}_{\gamma\delta}^{(i)}P_\gamma P_\delta+\sum_j b_{ij}q_j=0, \quad (i=1, 2, \cdots, 3N-6). \quad (17)$$

These may be solved for q_j, the values obtained substituted in Eq. (16), and the resulting expression for $\mu_{\alpha\beta}$ used in the equation for W_R. An equation corresponding to Eq. (14) but expressed in terms of $\bar{\mu}_{\alpha\beta}^{(i)}$ and b_{ij} rather than $\mu_{\alpha\beta}^{(k)}$ and λ_k will result.

If we introduce the symbol $\tau_{\alpha\beta\gamma\delta}$, W_R becomes

$$W_R=W_R^0+\tfrac{1}{4}\sum_{\alpha,\beta,\delta,\gamma}\tau_{\alpha\beta\gamma\delta}P_\alpha P_\beta P_\gamma P_\delta. \quad (18)$$

In terms of $\mu_{\alpha\beta}^{(k)}$ and λ_k, $\tau_{\alpha\beta\gamma\delta}$ is given by

$$\tau_{\alpha\beta\gamma\delta}=-\tfrac{1}{2}\sum_k \mu_{\alpha\beta}^{(k)}\mu_{\gamma\delta}^{(k)}/\lambda_k. \quad (19)$$

The Phase Integral for the Semi-Rigid Rotator *

The second term of Eq. (18) is a correction term, consequently its contribution to the exponential $e^{-W_R/kT}$ will be expanded as a power series.

$$e^{-W_R/kT}=e^{-W_R^0/kT}\Big[1-(1/4kT)\sum_{\alpha,\beta,\gamma,\delta}\times\tau_{\alpha\beta\gamma\delta}P_\alpha P_\beta P_\gamma P_\delta+\cdots\Big]. \quad (20)$$

It will be found sufficient to take the first two terms only. The phase integral, Eq. (3), then becomes

$$Q_R=Q_R^0-(2\pi^2/h^3kT)\sum_{\alpha\beta\gamma\delta}\tau_{\alpha\beta\gamma\delta}\int\int\int P_\alpha P_\beta P_\gamma P_\delta e^{-W_R^0/kT}dP_x dP_y dP_z. \quad (21)$$

For each set of values of $\alpha\beta\gamma\delta$, the integral factors, becoming

$$\int_{-\infty}^{\infty}P_x^r e^{-P_x^2/2A_0kT}dP_x\cdot\int_{-\infty}^{\infty}P_y^s e^{-P_y^2/2B_0kT}dP_y\cdot\int_{-\infty}^{\infty}P_z^t e^{-P_z^2/2C_0kT}dP_z \quad (22)$$

in which r, s, $t=0$, 1, 2, 3 or 4 with the condition that $r+s+t=4$. However, if r, s, or t is an odd integer, the corresponding integral vanishes. With r, s and t all even the integrals can be evaluated, with the result that

$$Q_R=Q_R^0(1+\rho T), \quad (23)$$

in which

$$\rho=-\tfrac{1}{4}k(3\tau_{xxxx}A_0^2+3\tau_{yyyy}B_0^2+3\tau_{zzzz}C_0^2+2\tau_{xxyy}A_0B_0+2\tau_{yyzz}B_0C_0+2\tau_{zzxx}C_0A_0+4\tau_{xyxy}A_0B_0+4\tau_{yzyz}B_0C_0+4\tau_{zxzx}C_0A_0). \quad (24)$$

The relations $\tau_{xyxy}=\tau_{yxxy}=\tau_{xyyx}=\tau_{yxyx}$, etc., have been used.

Consequently, the corrected expressions for F, S and C_v are

$$F=F'-\rho RT^2, \quad (25)$$

$$S=S'+2\rho RT, \quad (26)$$

$$C_v=C_v'+2\rho RT, \quad (27)$$

in which higher powers of ρT have been dropped. F', S' and C_v' represent the quantities calculated for the rigid rotator, plus the translational and vibrational contributions.

Numerical Results and Discussion

Table I shows the numerical values of ρ for several light molecules. These have all been calculated with the assumption of valence forces. It is seen from these results that the distortional correction is not entirely negligible in these light molecules, but that it may contribute a correction of as much as half a percent to the heat capacity in certain cases. For heavier molecules, however, the effect will be quite small.

Table I. *Values of ρ for several molecules.*[4]

	H_2O	H_2S	NH_3	CH_4	C_2H_4	
ρ	2.04	1.62	1.45	1.72	0.79	($\times 10^{-5}$)

Considerable experimental data exist on the heat capacity of steam, a summary of which is given by Keyes.[5] When the above correction is applied to Gordon's [6] calculated values of C_p^0, the agreement with the average of the experimental values is somewhat improved.

* In these computations it is assumed that the vibrational and rotational partition functions can be treated as independent, which is not, of course, strictly true.

[4] The experimental data used were: for H_2O, the force constants were taken from L. G. Bonner, Phys. Rev. **46**, 458 (1934); for H_2S, from P. C. Cross, Phys. Rev. **47**, 7 (1935); for NH_3, from J. B. Howard, J. Chem. Phys. **3**, 207 (1935); for CH_4, the fundamental frequencies listed by N. Ginsburg and E. F. Barker, J. Chem. Phys. **3**, 668 (1935); for C_2H_4, the force constants were taken from L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

[5] F. G. Keyes, L. B. Smith and H. T. Gerry, Proc. Am. Acad. Arts and Sciences, **70**, 319 (1936). These results have been multiplied by 18.0154/4.1833 to yield 15° cal./mole.

[6] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934). These results have been corrected to R = 1.9863.

Thermodynamic Properties of Phosphorus Compounds*

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With Raman spectrum, electron diffraction and existing equilibrium data the standard virtual entropies of P(*s*, white), $P_4(g)$. $PCl_3(g)$, $PCl_3(l)$, $PCl_5(g)$, and $PCl_5(s)$ are calculated to be 10.55, 66.88, 74.7, 52.8, 87.7, and 40.8 cal./deg. respectively. The corresponding standard free energies of formation are calculated to be (0), 5850, −64,650, −63,570, −72,540 and −77,950 cal., respectively.

INTRODUCTION

THE determination of the thermodynamic properties of phosporus compounds has been prevented by the lack of a reliable value for the entropy of solid white phosphorus. Attention should be called to the fact that low temperature specific heat data for elementary phosphorus do not exist. Because of the importance of phosphorus compounds it is highly desirable to have such information. Preliminary values for the entropy of white phosphorus, 14.9 and 15.5 cal./deg., were previously obtained[1] by dubious extrapolation of not too accurate high temperature equilibrium data; though in surprisingly good agreement with each other, the values seem to be too high.

In this paper is presented what is felt to be a reasonably reliable value for the entropy of phosphorus calculated from Raman spectrum, electron diffraction, and vapor pressure data. From this result, combined with heats of formation and certain equilibrium data, are calculated the thermodynamic properties of phosphorus trichloride and phosphorus pentachloride.

CALCULATIONS

Phosphorus vapor

It is known that at room temperature solid, white phosphorus, as well as the vapor above it, consists of P_4 molecules. Electron diffraction experiments have recently shown that the structure of the P_4 molecule is that of a regular tetrahedron with a *P–P* distance of 2.21A.[2] This leads to a moment of inertia of 248×10^{-40} g, cm.^{2}

The three vibrational frequencies of the P_4 molecule[3] have been found to be $\nu_1\{2\}=372(1)$, $\nu_2\{3\}=463(3)$, and $\nu_3\{1\}=607(6)$ cm^{-1}, where numbers in braces indicate the degeneracies of the respective modes of vibration, and numbers in parentheses indicate relative intensities. There should be little doubt concerning the assignment of frequencies since the ratios of the values agree with the ratios calculated by a central force treatment[4] as well as might be expected:

$$2\nu_1\{2\}=\sqrt{2}\nu_2\{3\}=\nu_3\{1\}.$$

Assuming that the molecule is a rigid, spherical top, that the vibrations are harmonic, and that interaction between vibration and rotation may be neglected, one may calculate the entropy of $P_4(g)$ by well-known methods.[5] Neglecting effects due to nuclear spin, one then gets for the virtual entropy of P_4 gas:

$$S_{298}{}^*P_4(g)=66.88 \text{ cal./deg.}$$

From the vapor pressures of solid white phosphorus as determined by Duncan and Macrae[6] we may write the equations:

$$4P(s, \text{ white})=P_4(g),$$
$$\Delta H_{298}=13{,}220 \text{ cal.}, \quad \Delta F^\circ_{298}=5{,}850 \text{ cal.}$$

The entropy of solid phosphorus

The above equations lead to the value 10.55 for the entropy of solid white phosphorus. This value should be considerably more accurate than that previously calculated. With its aid it is now possible to compute the thermodynamic

* Publication No. 551.

[1] D. M. Yost and T. F. Anderson, J. Chem. Phys. **2**, 624 (1934).

[2] Maxwell, Hendricks and Mosley, J. Chem. Phys. **3**, 699 (1935).

[3] Bhagavantam, Ind. J. Phys. **5**, 35 (1930); Venkateswaran, Proc. Ind. Acad. **3**, 260 (1935).

[4] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

[5] L. S. Kassel, J. Am. Chem. Soc. **55**, 1351 (1933); Chem. Rev. **18**, 277 (1936).

[6] Duncan and Macrae, J. Am. Chem. Soc. **43**, 547 (1921).

properties of any phosphorus compound whose entropy and heat of formation are known.

Phosphorus trichloride

The heats of formation[7] and vaporization[8] of PCl_3 are 75,900 cal. and -7620 cal., respectively, and the free energy of vaporization is 1080 cal. at 25°C. The entropy of $PCl_3(g)$ has been calculated[1] to be 74.7 cal./deg. One may then write:

$$P(s, \text{white})+3/2Cl_2(g)=PCl_3(l),$$
$$\Delta H=-75{,}900 \text{ cal.}, \quad \Delta F^\circ_{298}=-64{,}650 \text{ cal.},$$
$$P(s, \text{white})+3/2Cl_2(g)=PCl_3(g),$$
$$\Delta H=-68{,}280 \text{ cal.}, \quad \Delta F^\circ_{298}=-63{,}570 \text{ cal.}$$

Phosphorus pentachloride

Holland[9] has made careful equilibrium measurements on the reaction $PCl_3(g)+Cl_2(g)=PCl_5(g)$ over the temperature range 440°–630° and his results have been recalculated by Nernst.[10] The vapor pressures of $PCl_5(s)$ have been carefully measured by Smith and Lombard.[11] From these results, together with those obtained above, the following thermochemical equations may be written:

$$PCl_3(g)+Cl_2(g)=PCl_5(g),$$
$$\Delta H_T=-20{,}000-3.473\,T,$$
$$\Delta F_T^\circ=-20{,}000+7.99\,T\log_{10}T+17.27\,T,$$
$$\Delta H_{298}=-21{,}040 \text{ cal.}\ \Delta F_{298}^\circ=-8970 \text{ cal.},$$

$$PCl_5(s)=PCl_5(g),$$
$$\Delta H_T=30{,}763-38.144\,T,$$
$$\Delta F_T^\circ=30{,}763+87.83\,T\log_{10}T-302.36\,T,$$
$$\Delta H_{298}=19{,}390 \text{ cal.}, \quad \Delta F_{298}^\circ=5410 \text{ cal.},$$

$$P(s, \text{white})+5/2Cl_2(g)=PCl_5(g),$$
$$\Delta H_{298}=-89{,}316 \text{ cal.}, \quad \Delta F_{298}^\circ=-72{,}540 \text{ cal.},$$

$$P(s, \text{white})+5/2Cl_2(g)=PCl_5(s),$$
$$\Delta H_{298}=-108{,}706 \text{ cal.}, \quad \Delta F_{298}^\circ=-77{,}950 \text{ cal.}$$

From its heat of solution, Thomsen[12] obtained the value $-106{,}600$ cal. for the heat of formation of $PCl_5(s)$. The agreement is satisfactory.

If we take Giauque's[13] value, 53.31 cal./deg., for the entropy of $Cl_2(g)$, there is then obtained for the standard virtual entropies of $PCl_5(s)$ and $PCl_5(g)$, 40.8 and 87.7 cal./deg., respectively. An electron diffraction determination of the structure of PCl_5, combined with Raman data would lead to an independent determination of these quantities.

[7] Berthelot and Longuinine, Ann. d. chim. phys. (5) **6**, 307 (1875); Thomsen, Ber. **16**, 37 (1883); J. Ogier, Comptes rendus **87**, 210 (1878).
[8] Regnault, Mem. de. l'acad. Sciences (France) **26**, 339 (1862).
[9] C. Holland, Zeits. f. Elektrochemie **18**, 234 (1913).
[10] W. Nernst. Zeits. f. Elektrochemie **22**, 37 (1916).
[11] Alex. Smith and R. H. Lombard, J. Am. Chem. Soc. **37**, 2055 (1915).
[12] J. Thomsen, "Systematisk gennemförte termokemiske undersögelsers numeriske og teortiske resultater" (1882–1886). International Critical Tables, Vol. V, p. 180.
[13] Giauque, J. Am. Chem. Soc. **54**, 1731 (1932).

AUGUST, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

Atomic Dimensions from the Coefficients of Compressibility and Thermal Expansion

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(Received March 23, 1936)

Starting from the equation of state $p-K(V-V_0)/V_0=RT/V-V_0$, the relation $\alpha_a/\beta=R/(V-V_0)$ is derived, where V_0 is identified with the actual volume occupied by one mole of atoms or molecules. Values of the radii of atoms for different elements are calculated from this relation and compared to the values obtained from crystal analysis. Possibility of using the relation $\alpha_a/\beta=R/(V-V_0)$ to estimate molecular dimensions in the liquid state is also referred to.

THE estimation of the size of atoms or molecules from the van der Waals equation for gases

$$p+a/V^2=RT/(V-b) \qquad (1)$$

is well known. Here b represents 4 times the actual volume of the molecules in 1 mole, and may be calculated from the relation

$$b=RT_K/8P_K, \qquad (2)$$

where T_K and P_K are, respectively, the critical temperature and pressure.

A similar procedure for the calculation of atomic dimensions may also be pursued in the cases of solids or liquids if a proper equation of state for those substances is known. In a paper published about five years ago,[1] the writer then suggested an equation of state of the form

$$p-K(V-V_0)/V_0=RT/(V-V_0) \qquad (3)$$

for the liquid and solid states. Here p is the external pressure applied, V the molecular volume at absolute temperature T, V_0 the molecular volume at absolute zero, R the gas constant, and K an arbitrary constant.

If to a mass of molecular volume V two different pressures p_1 and p_2 are applied, we have evidently

$$\begin{aligned} p_1-K(V_1-V_0)/V_0&=RT/(V_1-V_0),\\ p_2-K(V_2-V_0)/V_0&=RT/(V_2-V_0). \end{aligned} \qquad (4)$$

Eliminating K from the Eqs. (4), we obtain

$$\begin{aligned} &p_1/(V_1-V_0)-p_2/(V_2-V_0)\\ &\quad=RT(1/(V_1-V_0)^2-1/(V_2-V_0)^2). \end{aligned} \qquad (5)$$

Since in the case of liquids and solids the compressibility is usually small, V_1 and V_2 can differ only by an insignificant amount for ordinary magnitudes of applied pressures. We may therefore write approximately V for both V_1 and V_2 and reduce (5) to the form

$$p_1-p_2=RT(V_2-V_1)/(V-V_0)^2. \qquad (6)$$

Multiplying both sides by V_2 and rearranging, we have

$$-V_2(p_1-p_2)/(V_1-V_2)=RTV_2/(V-V_0)^2. \qquad (7)$$

Denote the coefficients of compressibility and average thermal expansion respectively by β and α_a, it is seen that according to the usual definition, we have

$$\begin{aligned} 1/\beta&=-V_2(p_1-p_2)/(V_1-V_2);\\ 1/\alpha_a&=TV/(V-V_0)=TV_2/(V-V_0). \end{aligned} \qquad (8)$$

Eq. (7) becomes then

$$\alpha_a/\beta=R/(V-V_0);\quad \text{or}\quad V_0=V-\beta R/\alpha_a. \qquad (9)$$

Here α_a is to be noted as the average thermal expansion.

[1] G. F. Djang, "Physical Constants and Molecular Forces," Science J. of Univ. of Shanghai (1930).

As the thermal pressure $RT/(V-V_0)$ vanishes when T equals zero, it may be safely assumed that at that condition all the atoms (or molecules) are as closely packed as possible and that V_0 differs very little from the volume actually occupied by the atoms. If N is the Loschmidt number, the radius r of the atom may then be calculated as

$$r=\left[\frac{3V_0}{4\pi N}\right]^{\frac{1}{3}}=\left[\frac{3}{4\pi N}\left(V-\frac{\beta R}{\alpha_a}\right)\right]^{\frac{1}{3}} \qquad (10)$$

with possibly a small error. Values obtained thus are tabulated in Table I. A glance at the table shows clearly that the values of r_2 calculated from Eq. (10) agree with crystal data very well in spite of approximations.

Eq. (9) may also be applied to molecules in a liquid state. For spherical molecules, V_0/N gives directly an estimation of the radius of the

TABLE I. *Atomic radii from compressibility and expansion.*

ELEMENTS	α ($\times 10^5$ per deg.)	β ($\times 10^{12}$ c.g.s.u.)	V (cc)	V_0 (cc)	r_1 CRYSTAL DATA ($\times 10^{-8}$ cm)	r_2 CALCULATED ($\times 10^{-8}$ cm)
Na	22.0	15.4	23.7	17.63	1.92	1.91
K	25.0	31.5	45.4	33.90	2.36	2.36
Rb	30.0	40.0	56.25	41.16	2.53	2.54
Cs	28.3	61.0	71.0	53.0	—	2.76
Ca	7.1	5.5	25.3	18.71	1.97	1.94
P	36.0	20.3	17.0	12.3	—	1.70
Mg	7.8	2.7	13.3	10.02	1.60	1.60
Bi	4.0	2.8	21.2	14.95	—	1.81
Al	7.2	1.3	10.1	8.33	1.43	1.48
Cu	5.0	0.75	7.12	5.84	1.28	1.32
Cd	7.4	1.9	13.6	11.13	1.52	1.64
Fe	3.6	0.60	7.10	5.72	1.27	1.31
Ni	4.2	0.27	6.67	5.52	1.24	1.30
Co	$\alpha/\beta=68\times 10^6$		6.9	5.67	1.25	1.31
Zn	8.7	1.7	9.21	7.58	1.37	1.44
Mo	1.1	0.26	10.7	8.74	1.40	1.51
I_2	25.0	13.0	25.7	21.38	—	2.02
Ag	5.7	1.01	10.3	8.84	1.44	1.50
Pt	2.7	0.40	9.12	7.89	1.38	1.46
Tl	9.0	2.6	17.2	14.79	1.71	1.80
Pb	8.8	2.2	18.3	15.99	1.74	1.85
Pd	3.8	0.58	9.24	8.01	1.37	1.47
Au	4.3	0.60	10.0	9.09	1.44	1.53
Li	19.0	8.8	13.0	9.01	1.57	1.52
Sb	3.3	2.2	18.1	12.56	—	1.70
S	18.0	12.5	15.5	9.73	—	1.57

α = Coefficient of thermal expansion.
β = Coefficient of compressibility.
V = Gram molecular vol. at T = 290°C.
V_0 is Gram molecular vol. calculated from Eq. (9).
α for the temperature range 0→100°C is used instead of α_a as defined in Eq. (8), because values of the latter are unavailable.
r_1 are taken from the data cited by V. M. Goldschmidt in the paper "Crystal Structure and Chemical Constitution." J. Faraday Soc., March (1929). Values of r from different authorities often differ somewhat.
α, β, and V are taken from *Smithsonian Physical Tables.*

individual molecules. For molecules of a non-spherical shape, V_0/N can help at least to determine one dimension of the molecules. For instance, in the case of ring or chain form compounds, the value V_0/N gives the length of the chain or the size of the ring when the depth of the molecule in question is known, or *vice versa*. Further data are being gathered in this direction.

Discussion

From the conception of spherical atoms used in the derivation of Eq. (10), the value r calculated from $[3V_0/4\pi N]^{\frac{1}{3}}$ should be appreciably larger than the real radius of the atom. Therefore it is rather surprising that the agreement between the calculated values and the crystal data should be as close as indicated in the table. The agreement is perhaps due to the fact that at absolute zero temperature the actual dimensions of the atoms are so reduced that this reduction just about counterbalances the additional part included in V_0. Anyhow, though theoretical explanations may be yet to be found, the formula seems to be proving a very helpful guidance in the work of crystal analysis.

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The Structure of Rubrene and Some Remarks on the "Ortho-Effect"

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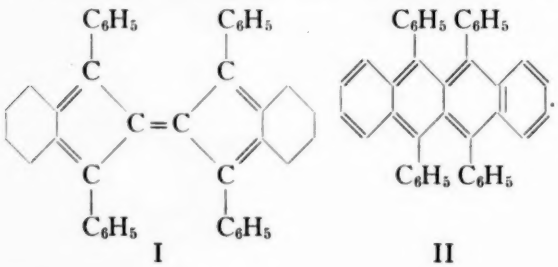
(Received April 22, 1936)

Recently W. H. Taylor[1] has described x-ray measurements of rubrene, modification B. The data

C_{2h}^5 $a=17.9$A, $b=10.1$A, $c=8.8$A, $\beta=120°$; $n=2$;

plane of the molecule nearly parallel to (010);

have been found. As Taylor pointed out, they are compatible with the rubrene formula (I), originally developed by Moureu and his co-workers.[2] Meanwhile the experiments of Eck and Marvel[3] and of Koelsch and Richter[4] have shown that formula (I) cannot be correct, and recently Dufraisse and Velluz[5] have proved that rubrene has structure (II); the same conclusion was reached by experiments in our laboratory, which will be reported elsewhere.



I II

Is it possible to reconcile formula II with the x-ray data? Consideration of the models corresponding to I and II reveals that the available x-ray data cannot give an exclusive proof for one of the two formulae; but packing of the molecules I into a three-dimensional structure with the above parameters seems more complicated. Therefore, also from x-ray data, formula II seems more likely (Figs. 1–4). The model of II still allows for two possibilities, but only the second one (II_2) of them leads in a simple way to the arrangement C_{2h}^5.

It may be noted that the formation of rubrene-peroxide is in accordance with formula II. The model shows that between the positions 9 and 10 of the anthracene nucleus a bridge of two carbon or similar atoms (e.g., oxygen) may be extended without any strain.[6] The peroxide of rubrene, therefore, is the next analog of the peroxides of

[1] Taylor, Zeits. f. Krist. **A93**, 151 (1936).
[2] Willemart, Comptes rendus **187**, 385 (1928); Moureu, Dufraisse and Enderlin, ibid., p. 406.
[3] Eck and Marvel, J. Am. Chem. Soc. **57**, 1898 (1935).
[4] Koelsch and Richter, J. Am. Chem. Soc. **57**, 2010 (1935).
[5] Dufraisse and Velluz, Comptes rendus **201**, 1394 (1935).
[6] Compare Bergmann and Fujise, Liebig's Annalen 480. 188 (1930); Diels and Alder, Liebig's Annalen **486**, 191 (1931); Ber. d. D. Chem. Ges. **64**, 2117 (1931); Clar, Ber. d.

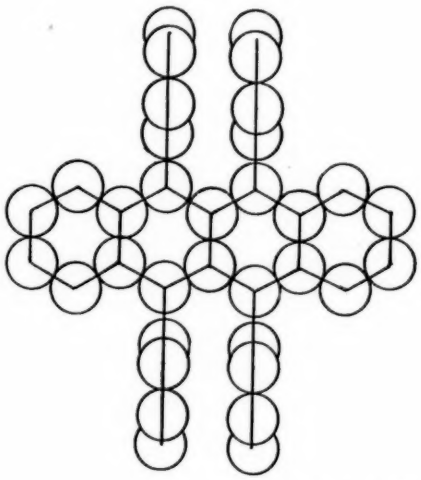


FIG. 1. Formula II_1 (phenyl groups ⊥).

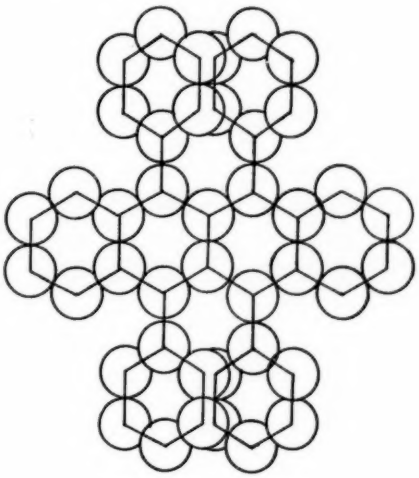


FIG. 2. Formula II_2 (phenyl groups crossed).

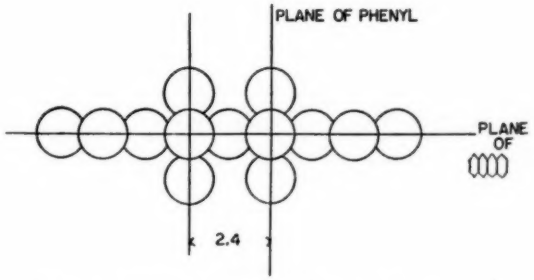


FIG. 3. Formula II_1 (projection ⊥ Fig. 1).

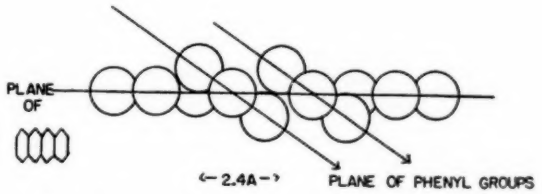


FIG. 4. Formula II_2 (projection ⊥ Fig. 2).

anthracene, or 9.10-diphenylanthracene, recently described by Dufraisse, Gérald and Étienne.[7] The most important feature of the above structure is that the molecule *is no longer flat.* The volume of the phenyl substituent groups prevents any plane arrangement. This arrangement is the reason for the value 10.1A of the *b* axis. Naphthacene itself should be morphotropic to naphthalene and anthracene; only the length *c* of the molecule should vary (2.4A more than anthracene), but the other dimensions should be identical.

There is another known case, where substituents of an aromatic system are not situated in the ring plane, namely, *m*-dinitrobenzene;[8] here, the oxygen atoms lie in two planes parallel to the plane of the hexagon, which contains naturally also the nitrogen atoms. While in the case of rubrene the reason for the deviation is obvious, for *m*-dinitrobenzene no structural explanation can be given. But it might be expected that *o*-dinitrobenzene or 1.8-dinitronaphthalene show a bent structure due to the same reasons as valid in the case of rubrene.

If two *ortho* substituents are too bulky for a normal arrangement in the plane of the nucleus, two possibilities may be foreseen theoretically:

(a) The substituents, which in this case must be polyatomic, undergo a rotation so as to arrange in a plane bent or perpendicular to that of the nucleus. This occurs apparently in the case of rubrene and perhaps in the case of

D. Chem. Ges. **64**, 1676, 2194 (1931); Schönberg, Trans. Faraday Soc. **32**, 514 (1936). It is noteworthy, that according to Bistrczycki and co-workers (Helv. Chim. Acta **5**, 20 (1922); **7**, 935 (1924)) *one* sulfur atom is able to form a bridge between the positions 9 and 10 of the anthracene system. That is perhaps due to the greater volume of the sulphur atom.

[7] Dufraisse and Gérald, Comptes rendus **201**, 428 (1935); Dufraisse and Étienne, ibid., p. 280. Compare Willimart, ibid., p. 1201; **202**, 140 (1936).

[8] Hendricks and Hilbert, J. Am. Chem. Soc. **53**, 4280 (1931).

1.8 dinitronaphthalene, where the dipole moment indicates such a deviation. The "normal" dipole moment has been explained accordingly by E. Bergmann and J. Hirshberg.[9]

(b) The valency angle between the substituents is widened so as to increase the distance between the substituents. This effect has been discussed by Bergmann and Engel[10] and its reality has been demonstrated—at least qualitatively—by Hendricks, Maxwell, Mosley and Jefferson,[11] by Schopp and Wolf[12] in the case of *o*-diiodobenzene and by de Laszlo[13] in the case of *o*-diiodobenzene and 1.8 diiodonaphthalene.

The above considerations suggest the x-ray investigation of a series of substances. Experiments in these directions are now in progress.

[9] Bergmann and Hirshberg, J. Chem. Soc. 331 (1936).
[10] Bergmann and Engel, Zeits. f. physik. Chemie **B8**, 111; **B10**, 106 (1930).
[11] Hendricks, Maxwell, Mosley and Jefferson, J. Chem. Phys. **1**, 549 (1933).
[12] Schopp and Wolf, Chem. Zentralblatt **2**, 2040 (1935).
[13] De Laszlo, Trans. Faraday Soc. **30**, 892 (1934).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($5.00 per page) will not be made and no reprints will be furnished free.

The Raman Spectra of Deutero-acetones and Methyl Alcohol-*d*

Raman spectra have been photographed for a series of equilibrium solutions of the several deutero-acetones produced by means of the exchange reaction of acetone with deuterium oxide[1] and containing progressively higher deuterium fractions up to 91 percent. The results are summarized in Table I, from which the changes of frequency may be seen as a function of the isotopic composition.

TABLE I

Acetones (percent D)	0	4	24	51	70	91
Raman Frequencies (cm^{-1})	396		402	396	393	
	531	533	532	502	484	488
			760	714	702	706
	796	790	794	750	744	
	1068	1067	1047	1036	1030	1031
	1706	1707	1703	1703	1700	1704
					2060	2049
		2175	2163	2126	2104	2072
			2182	2157	2151	2113
			2218	2222	2210	2160
	2918	2930		2256	2248	2219
	2970	2963	2934	2942	2948	2251
	3000	3001	2997	2992	3000	2937

As the deuterium fraction increases, the higher frequency of acetone at 2918 cm^{-1} and possibly the frequencies 2970 and 3000 cm^{-1}, increase slightly and then fade out, only the high probability parallel frequency at 2937 cm^{-1} appearing faintly in the most concentrated *d*-acetone. Simultaneously, at deuterium fraction = 4 percent, a line appears at 2175 cm^{-1} and three are found in this region when D = 24 percent. The strong lines at about 2115, 2160, 2219 and 2250 cm^{-1} appear at higher deuterium concentrations, with 2113 cm^{-1} becoming the strongest line at the greatest deuterium concentration; weak lines at 2049 and 2072 cm^{-1} also appear in the D = 91 percent acetone. The 1706 cm^{-1} line, ascribed to C = 0, appears quite unchanged in all the acetones. The 795 cm^{-1} line splits in the intermediate acetones to give a second line at 760 cm^{-1}. This second line becomes strong, splits to give a third at about 700 cm^{-1} with the original line at 795 cm^{-1} disappearing. Finally, the 750 cm^{-1} line fades, leaving in the most concentrated *d*-acetone the 700 cm^{-1} as the strongest line. Lines at 531 cm^{-1} and 1069 cm^{-1} are gradually displaced toward the exciting line as the concentration of deuterium is increased.

We are attempting to interpret these results by the use of the equations of Rosenthal,[2] comparing the data with frequencies calculated for the four possible isotopic methyl groups.

The line observed at 2970 cm^{-1} with ordinary acetone is at present unexplained, CH_3 having theoretically only two frequencies near 3000 cm^{-1}.[3] The usual explanation of resonance degeneracy apparently is not tenable in this case. The presence of the four strong and two weak lines at 2000–2250 cm^{-1} in the acetones having the greatest deuterium fraction is also of interest, since never more than the 3 hydrogen lines from 2900–3050 cm^{-1} appear in the acetones containing little deuterium.

Strong Raman lines appeared in acetone at 1157, 1224, 1340 and 1428 cm^{-1}. Lines at about these frequencies occur in the intermediate deutero-acetones and practically disappear in the 91 percent deutero-acetone. We have not tabulated these lines, however, because they may be due to excitation by the 4047 and 4078A lines of the mercury source. This point is being studied further.

The Raman spectra of methyl alcohol and methyl alcohol-*d* have been determined, using the mercury lines at 4358 and 2536A as exciting sources. Table II presents

TABLE II.

CH_3OH (cm^{-1})		CH_3OD (cm^{-1})	
From 2536	4358	2536	4358
1033	1031	1031	1034
	1056		1071
1109	1119	1153	1154
1153	1171		1179
1464	1451	1382	1370
2835	2839	2494 (Band)	2494 (Band)
2913	2914	2836	2839
2954	2948	2915	2918
2992	2982	2946	2947
3388 (Band)	3415 (Band)	2989	2986

the lines found. The OD band occurs at 2500 $cm^{-1} \pm 10$ and the OH band at 3400 $cm^{-1} \pm 20$.[4] A line at about 1375 cm^{-1} in the CH_3OD spectra and one at 115 cm^{-1} in the CH_3OH were other differences noted. The four lines between frequencies 2840 and 3000 cm^{-1} are very strong.

J. R. BATES
LEIGH C. ANDERSON
J. O. HALFORD

University of Michigan,
Ann Arbor, Michigan,
July 6, 1936.

[1] Halford, Anderson and Bates, J. Am. Chem. Soc. **56**, 491 (1934); Halford, Anderson, Bates and Swisher, ibid., **57**, 1663 (1935).
[2] Rosenthal, Phys. Rev. **47**, 235 (1935).
[3] Adel and Barker, J. Chem. Phys. **2**, 627 (1934).
[4] Redlich and Pordes, Naturwiss. **22**, 808 (1934).

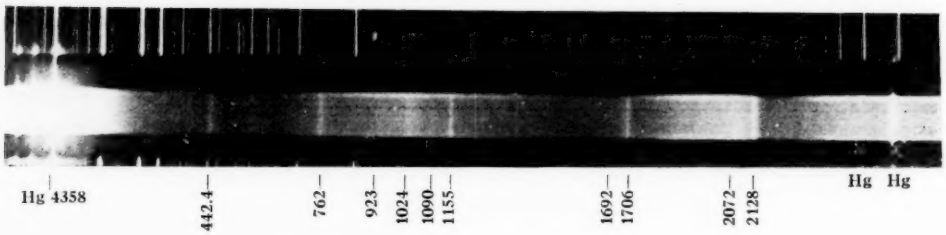


FIG. 1.

Raman Spectrum of Deutero-Acetaldehyde

The Raman spectrum of a very pure sample of deutero-acetaldehyde sent to me by Professor Zanetti of Columbia University was photographed with the large prism spectrograph of 1 meter focus described in earlier papers. Excitation was by Hg 4358, filters of sodium nitrite and praseodymium being employed, the latter to remove the continuous background of the arc between 4358 and 4915 which was rather strongly scattered. The first spectrum taken indicated that some fluorescent light was present which blotted out all but the strongest lines. An exposure to unfiltered light for some hours destroyed the impurity causing fluorescence and a very satisfactory spectrum was obtained, which is reproduced in Fig. 1. The discontinuities in the continuous spectrum are of course due to the selective absorption of the praseodymium.

The wave number differences of the lines are given in Table I.

TABLE I.

Deutero-acetaldehyde V	Acetaldehyde (Kohlrausch and Keppe[1])
422.4	512
762	887
1024	914
1090	1111
1153	1352
1692	1392
1706	1428
2072	1715
2128	2732
	2836
	2915
	2966
	3005

The tube, of fused quartz provided with a flat polished window of the same material was filled for me by Professor Zanetti. Publication of this note has been delayed for three months as it was hoped that deutero-paraldehyde would soon be ready for examination.

R. W. WOOD

The Johns Hopkins University,
Baltimore, Maryland,
June 22, 1936.

The Dipole Moments of the Alkali Halides

In our paper on the measurement of dipole moments of the alkali halides,[1] a discussion of the uncertainties in the electric field strength was inadvertently omitted. This was unfortunate, since the possibility exists of considerable error in this quantity. The important question is whether the error could be great enough to account for the discrepancy between our results and those of Scheffers.[2] This does not appear to us to be probable, but it would be desirable to repeat the measurements with a more satisfactory source of d.c. high potential.

The difficulty with the transformer and kenetron as a source of potential is that the effective potential on the Rabi plates varies with the amount of leakage current. The only direct method of measuring the potential on the Rabi plates is by the use of a spark gap. The results of this method, while reproducible, are too uncertain to be satisfactory. It is, of course, possible to observe the peak voltage and wave form of the transformer itself with an oscillograph, and this has been done. The difficulty arises in determining the leakage current under operating conditions. The charging current through the kenetron was small, but not zero, so that the effective voltage was estimated at something less than the peak voltage. If the peak voltage were actually maintained on the plates, which would mean no leakage current, our moments as calculated would be about 20 percent too high. It appears to us to be very unlikely that this is the case. The most probable values for our results are those that are published. It is suggested there that the uncertainty was at least 10 percent. If weight is given to the results of Scheffers and certain theoretical considerations, one might suspect that our results are perhaps too high by this amount, but it does not appear possible to account for the difference between our results and those of Scheffers, solely on the basis of errors in our work.

W. H. RODEBUSH

Department of Chemistry,
University of Illinois,
Urbana, Illinois,
June 22, 1936.

[1] W. H. Rodebush, L. A. Murray, Jr. and M. E. Bixler, J. Chem. Phys. **4**, 372 (1936).
[2] H. Scheffers, Physik. Zeits. **35**, 425 (1924).

Preliminary Note on the Phase Relationships in the Nickel-Tin System

Because of the great industrial importance of the bronzes the constitutional diagram of the copper-tin alloys has been the subject of a large number of investigations. In the so-called nickel bronzes which are ternary alloys of copper, nickel and tin, the phenomenon of precipitation hardening is observed in certain ranges of composition. A knowledge of the phase relationships in the binary system nickel-tin is essential for the understanding of this phenomenon. It is therefore somewhat surprising that no complete x-ray investigation has as yet appeared in the international literature.

In connection with an investigation of the nickel bronzes we have made a complete examination of the nickel-tin system by x-ray methods. Because of its general interest we are communicating a brief summary of the more important phase relationships in what follows. A complete discription of our methods and results will appear in a later publication. Our results differ considerably from the results of earlier investigators who used the methods of thermal analysis and microscopic examination.

1. The investigation of the Ni-Sn system has been extended beyond the solubility limit of Sn in Ni already reported by the authors.[1]

2. The next phase to the nickel solid solution phase occurs at the composition Ni_3Sn. This phase has a very narrow composition range.

3. The Ni_3Sn phase is in equilibrium with a phase having a typical nickel arsenide structure between approximately 25.0 and 37.5 atomic percent tin.

4. The nickel arsenide structure first appears alone at about 37.5 atomic percent Sn but extends as a homogeneous phase only up to 45 atomic percent Sn. It thus requires excess nickel atoms to stabilize the lattice.

5. At 40 atomic percent Sn or the composition Ni_3Sn_2, a new phase forms from the nickel arsenide-like phase at temperatures below 500°C. Its diffraction pattern appears to be closely related to the nickel arsenide structure and it may be a deformed modification. The range of homogeneity must be quite small since it is not found at 38.0 nor at 42.5 atomic percent Sn.

6. The homogeneity range of the NiAs-structure is independent of temperature on the high tin side but increases slightly at higher temperatures on the high nickel side.

7. In the remainder of the system there are three new phases provisionally called eta, theta and zeta. The first two have very narrow homogeneity ranges at approximately 51 and 54 atomic percent Sn, respectively. The eta phase forms by a peritectoid reaction between the NiAs-structure and theta. The zeta phase extends between approximately 56 and 62 atomic percent Sn although this range may possibly be more complicated.

8. The zeta phase coexists with the tin phase from 62 percent up to practically 100 percent Sn. The diffraction patterns indicate that the solubility of nickel in tin is very low.

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[1] E. R. Jette and E. Fetz, Metallwirtschaft **14**, 165 (1935).